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THE UNIVERSITY OF ALBERTA

VAPOUR - LIQUID EQUILIBRIA IN  
HYDROGEN SULPHIDE - NORMAL BUTANE SYSTEMS

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES IN  
PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE  
DEGREE OF MASTER OF SCIENCE IN PETROLEUM

ENGINEERING

DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

BY

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JANUARY, 31, 1963



## ABSTRACT

A review of the results published for systems containing hydrogen sulphide or normal butane is presented along with a brief description of some theoretical approaches to the prediction of vapour - liquid equilibrium. The thesis also contains a short description of the experimental equipment and the modifications required for the study of the hydrogen sulphide - normal butane system.

The vapour - liquid equilibrium of the binary system hydrogen sulphide - normal butane was studied at six temperatures, 125°F., 175°F., 200°F., 225°F., 250°F., and 275°F., over a range of pressure from 50 psia. to 1180 psia. No azeotropes were present at any of the temperatures studied but a definite trend toward a minimum boiling azeotrope did appear. The critical locus for the system was defined by three experimental points from this work and the critical properties of the pure components. The results are presented as tabulated data and graphs.

Equilibrium ratios were calculated at selected temperatures and pressures. These values were compared with those prepared by the Natural Gasoline Association of America for two convergence pressures, and with those calculated for other hydrocarbon - hydrogen sulphide binaries. The first comparison indicated the NGAA equilibrium ratios could be applied for normal butane in mixtures



with hydrogen sulphide. The second comparison showed the change in tendency toward azeotropic behaviour as the molecular weight of the paraffin hydrocarbon in binary mixtures with hydrogen sulphide changed.



## ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks to Dr. D. B. Robinson, Head of the Department of Chemical and Petroleum Engineering, University of Alberta, for his guidance, encouragement and helpful criticism during the course of this project.

Acknowledgement of debt is made to the California Standard Oil Company for their fellowship and to the National Research Council and Imperial Oil Company for their financial assistance. Thanks are extended to Mr. F. Butz and his staff for their cooperation in modifying the equipment and to all those friends and colleagues who contributed their time and thoughts to the solution of problems associated with this thesis.



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## A. INTRODUCTION

During the nineteenth century physicists and chemists first became interested in the behaviour of liquids and their associated gases. At that time attention was mainly focused on pure compounds. Later, interest spread to mixtures of two or more compounds. During the 1930's the marked increase in production of complex hydrocarbon mixtures from oil and gas reservoirs provided the impetus for an even more detailed analysis of phase behaviour and related phenomena.

At the present time, information available on this subject, though elaborate, is incomplete. It includes extensive experimental vapour - liquid equilibrium data, methods of obtaining such data, and methods for predicting the behaviour of specific systems. The data involve many pure paraffin hydrocarbons and mixtures of these in binary, ternary or more complex hydrocarbon mixtures. Some data are also available for mixtures of hydrocarbons with non-hydrocarbons such as hydrogen sulphide, carbon dioxide, or other compounds which may be found in oil and gas reservoirs.

The various methods of studying the equilibrium conditions are described in the extensive literature on the subject. Several of these are well summarized by Robinson and Gilliland (29). At the University of Alberta, a phase equilibrium cell was constructed during 1961. A detailed description of this cell has been presented by Sandercock (35).

The methods of predicting vapour - liquid equilibria include applications of equations of state and empirical correlations. An example of an equation of state is the equation presented in 1940 by



Benedict, Webb, and Rubin (2). Through the application of thermodynamic principles such equations may be applied to the prediction of vapour - liquid equilibria (3). Empirical correlations generally employ equilibrium ratios. For example, the methods proposed by Edmister (7), Hadden and Grayson (8), Lenoir and White (15), and Winn (36) all involve correlations of these ratios.

The intention of this investigation was;

1. to modify the existing equipment,
2. to employ the equipment in the determination of vapour - liquid equilibrium data for the system hydrogen sulphide - normal butane at a series of suitable temperatures,
3. to calculate, from the experimental data, equilibrium ratios for the system, and
4. to compare these equilibrium ratios with other values appearing in the literature for related systems.



## B. THEORY

### 1. PREVIOUS WORK

Many authors have studied hydrogen sulphide and normal butane as pure liquids and gases or in combination with other compounds. Pressure, volume, temperature data for pure hydrogen sulphide were presented in 1948 by West (37) and in 1950 by Reamer, Sage and Lacey (23). Similar data for normal butane were published in 1950 by Sage and Lacey (34).

Several binary systems containing hydrogen sulphide have been studied and reported. Data were presented in 1951 by Reamer, Sage and Lacey (24) for the system hydrogen sulphide - methane. This system did not exhibit an azeotrope at the temperatures studied by these authors nor at the lower temperatures investigated by Kohn and Kurata (13).

The combination of hydrogen sulphide with the next compound in the paraffin series, ethane, was shown to exhibit azeotropic behaviour by Kay and Brice (19). The azeotrope occurred at compositions high in ethane. The system hydrogen sulphide - propane (1,12) also exhibited an azeotrope. In this case, the azeotrope was formed at high hydrogen sulphide concentrations. As the critical conditions were approached the azeotropic composition increased in hydrogen sulphide concentration. In both mixtures the azeotrope corresponds to a minimum boiling condition.

Further data involving paraffin hydrocarbons leave a gap in the



scale of ascending molecular weight since the next system reported is hydrogen sulphide - normal pentane (25). In this case an azeotrope did not exist and the phase behaviour was typical of nearly ideal binary systems. Similarly, the system normal decane - hydrogen sulphide was shown (26) to exhibit no unusual characteristics.

Since the mixtures of hydrogen sulphide with normal pentane and normal decane do not demonstrate any unusual behaviour, and since the system propane - hydrogen sulphide does, the important gap involves systems of hydrogen sulphide with normal or iso-butane rather than the systems involving heavier hydrocarbons. Lenoir (16) presented comparisons of critical loci for systems containing azeotropes. The results presented seemed to indicate that if the critical temperatures of the two components were sufficiently close, azeotropes would be formed. In the case of the system hydrogen sulphide - normal butane the two critical temperatures are approximately  $99^{\circ}\text{F}$ . apart, whereas in the case of the ethane - hydrogen sulphide binary, a spread of about  $122^{\circ}\text{F}$ . exists. From this reasoning it would not be unreasonable to expect an azeotrope in the system hydrogen sulphide - normal butane.

Other data available on hydrogen sulphide systems include combinations with carbon dioxide (4, 14), and water (36) as binary systems, and a ternary mixture of hydrogen sulphide, methane and carbon dioxide (28, 30).



Considerable work has been done on systems involving normal butane. The binary systems of normal butane with methane (18, 20, 22, 27, 31, 32, 35), ethane (9), propane (21), and iso-butane (33) have been investigated. In none of these binary systems did any azeotrope appear. The phase behaviour in all cases was typical of simple binary systems. Other experimental data have been presented for ternary systems and mixtures of normal butane with non-hydrocarbons. Unusual results occurred for the system normal butane - ammonia (11). For this system an azeotrope appeared. The system normal butane - hydrogen was shown (1) to involve retrograde condensation of the second kind.

It is apparent that systems containing either hydrogen sulphide or normal butane can exhibit abnormalities, but the literature does not report any studies of the two compounds in the presence of each other. This leads to considerable speculation as to what the phase behaviour of such a binary system is.

## 2. PHASE BEHAVIOUR

A phase is a homogeneous, mechanically separable portion of a system. Provided that the temperature, pressure, and composition are the only limiting variables, Gibbs' Phase Rule may be applied to the system as follows:

$$F = C - N + 2$$

This rule relates the number of degrees of freedom,  $F$ , to the number of components,  $C$ , and the number of phases,  $N$ .



This study is concerned with two components, hydrogen sulphide and normal butane, with two phases present, a gaseous phase and the more dense liquid phase. Therefore, to define the system completely, two intensive variables such as temperature and pressure must be specified. This means that at a given temperature and pressure in the two phase region, the composition of the two phases present will be invariant.

A pair of liquids with molecules identical in size, which mix without the complicating effects of molecular association or chemical combination, would obey Raoult's Law:

$$P_i = P_{Vi} \cdot x_i \quad (1)$$

where  $P_i$  is the partial pressure of the  $i^{\text{th}}$  component over the solution,  $x_i$  is its mole fraction in the solution, and  $P_{Vi}$  is the vapour pressure of the  $i^{\text{th}}$  component in its pure state at the same temperature. The assumptions of identical molecules, and mixing without side effects cause deviations that may be either positive or negative.

Dalton's Law states that the total pressure of a gas is equal to the sum of the partial pressures of the components present. The common form of the law assumes the perfect gas laws apply, and may be written;

$$P_i = y_i \cdot P \quad (2)$$

where  $y_i$  is the mole fraction of the  $i^{\text{th}}$  component in the gas phase, and  $P$  is the total pressure of the system. Again deviations are



expected because of the assumption of an idealized system.

The combination of Raoult's and Dalton's Laws results in the equation;

$$y_i P = x_i P_{vi} \quad (3)$$

Thus, fixing the temperature and the total pressure defines the relationship between the gas and the liquid compositions.

Another useful concept is that of an ideal solution. By definition

and  $f_{il} = f_i \cdot x_i \quad (4)$

$$f_{ig} = f_i \cdot y_i \quad (5)$$

where  $f_i$  is the fugacity of a component in the gas, subscript g, or the liquid, subscript l, solution, and  $f_i$  is the fugacity of a component in the pure state at the temperature and pressure of the equilibrium system. For this definition to hold, it is required that component volumes be additive, internal energies be additive, and that no chemical effects take place upon mixing. At equilibrium the fugacity of a given component is the same in all phases, therefore equations 4 and 5 may be combined to give;

$$y_i/x_i = f_{il}/f_{ig} \quad (6)$$

In this case fugacities have replaced the pressures in equation 3.

These idealized approaches are not truly descriptive. Major deviations may be expected when the molecular volumes of the components are different or when disparities in the molecular forces are present. However, both approaches lead to the concept of an equilibrium ratio,  $K$ , of the form;

$$K_i = y_i/x_i \quad (7)$$



This equilibrium ratio provides a very useful method of correlating equilibrium data. Such data have shown the value of "K" for any component to be a function of the temperature, the pressure, and the composition of the system. The temperature and pressure parameters do not present any difficulty. The composition parameter does and considerable work has been done in defining the convergence pressure as the correct parameter. By definition, for a binary system the convergence pressure is the critical pressure of a mixture of the same components having a critical temperature equal to the working temperature of the system. For ternary systems such a definition loses its significance because a range of pressures are included in the definition. The addition of more components makes the situation even more complex. This has led to a more general concept of convergence pressure, namely that it is the pressure at which the equilibrium ratios for all components become unity at the system temperature.

Many methods have been presented to calculate this convergence pressure (8, 15, 36). Generally the methods involve the construction of a pseudo-binary system and a reversion to the original definition of the convergence pressure. For mixtures of paraffin hydrocarbons the equilibrium ratios calculated using convergence pressures are generally good. However, the addition of other compounds such as hydrogen sulphide may destroy the usefulness of the convergence pressure by adding another variable not accounted for by the convergence pressure.



Empirical equations of state may also be applied to studies of vapour - liquid equilibrium. For example the Van Laar (29) equation may be used for calculating vapour - liquid equilibrium. In deriving his equation Van Laar assumed that;

1. the excess partial molal entropy is zero,
2. there is no volume change upon mixing,
3. the Van der Waals' equation of state applies to each of the components and to mixtures of them as both liquids and vapours, and
4. the Van der Waals' constants for the mixture can be calculated from the constants for the pure components.

Another example of the application of an equation of state is the application of the Benedict, Webb, Rubin equation through the definition of fugacity. In this case the following assumptions are necessary;

1. the Benedict, Webb, Rubin equation applies to each of the components and to mixtures of them as both liquids and vapours, and
2. the eight constants necessary for the equation are known for the pure components and constants for the mixture can be calculated from these values.



## C. THE EXPERIMENTAL STUDY

### 1. EXPERIMENTAL APPARATUS

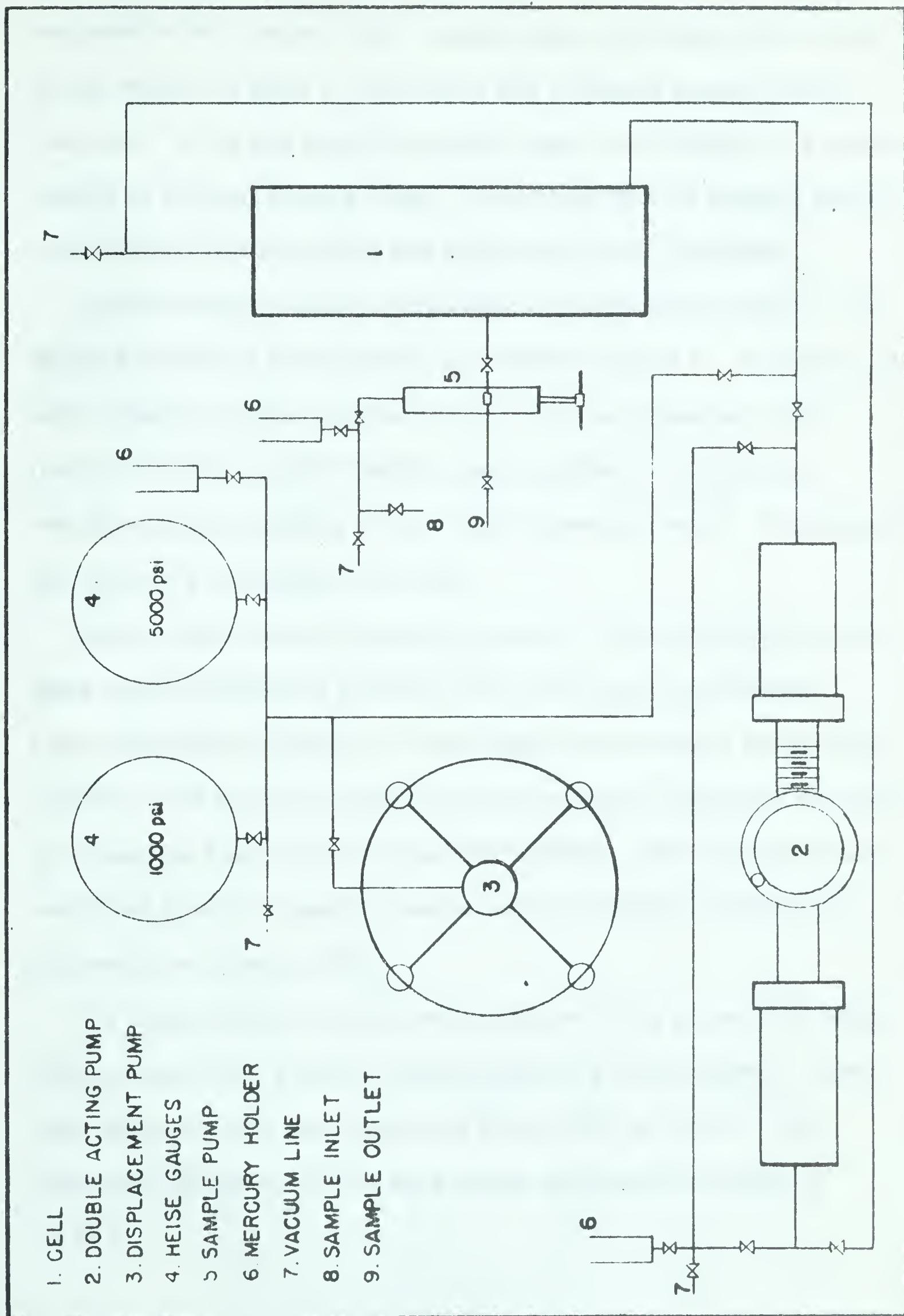
A very complete and detailed description of the vapour - liquid equilibrium cell was presented by Sandercock (35). Basically it was a windowed cell of variable volume. The schematic arrangement of the cell and its associated equipment is shown in Figure 1. Two important design features made this cell different from others which have been used for similar purposes.

First, the position of the meniscus can be changed without a change in sample volume. This was accomplished by means of the double acting pump shown in Figure 1. This pump removes mercury from one end of the cell at the same rate that mercury is added to the other. Thus, the sample contained between a piston and the mercury, can be moved to the desired level in the cell.

The second design feature was the addition of a small port below the window inside the cell. Mercury or liquid sample can be sprayed through this port and into the gas phase to bring the sample to equilibrium. This proved to be a very efficient way of obtaining equilibrium in a relatively short time. Some difficulty was encountered when very small liquid samples were present. In this case considerable time was required to allow the liquid to drain down the cell walls after spraying.

Samples were taken from a port at the window level and through the sample pump shown on Figure 1. Since considerable difficulty had been





Figure#1 Schematic diagram of equipment



encountered with the seal in the sample pump, the design was changed to that shown in Figure 2. Previously (35) a Humble packing design was used. In the new pump the packing rings were designed in a fashion similar to Chevron packing rings. It was found that the changed packing outlasted the Humble packing and as such was more applicable.

Another change was the modification of the periscope design. The detailed drawing of these units is presented in Figure 3. The periscopes were rebuilt to prevent any lens contact with the temperature bath fluids and to decrease the length of seal required. This approach was found to be mandatory for any high temperature work. It eliminated the need for a transparent bath fluid.

Several other minor changes were made. The most significant of these was the addition of a teflon O-ring seal below the neoprene ring on the piston in the cell. This change was necessary because the reaction of the hydrogen sulphide with the neoprene caused the neoprene to become hard and brittle, almost like bakelite. The neoprene seals would last about one month in contact with the hydrogen sulphide at temperatures of about  $125^{\circ}$  F.

The temperature of the cell was measured using an iron-constantan thermocouple and a Leeds-Northrup Model K-2 potentiometer. These units had previously been calibrated from  $-10^{\circ}$  C. to  $200^{\circ}$  C. This calibration was used for this work giving an expected accuracy of  $\pm 0.02^{\circ}$  C.



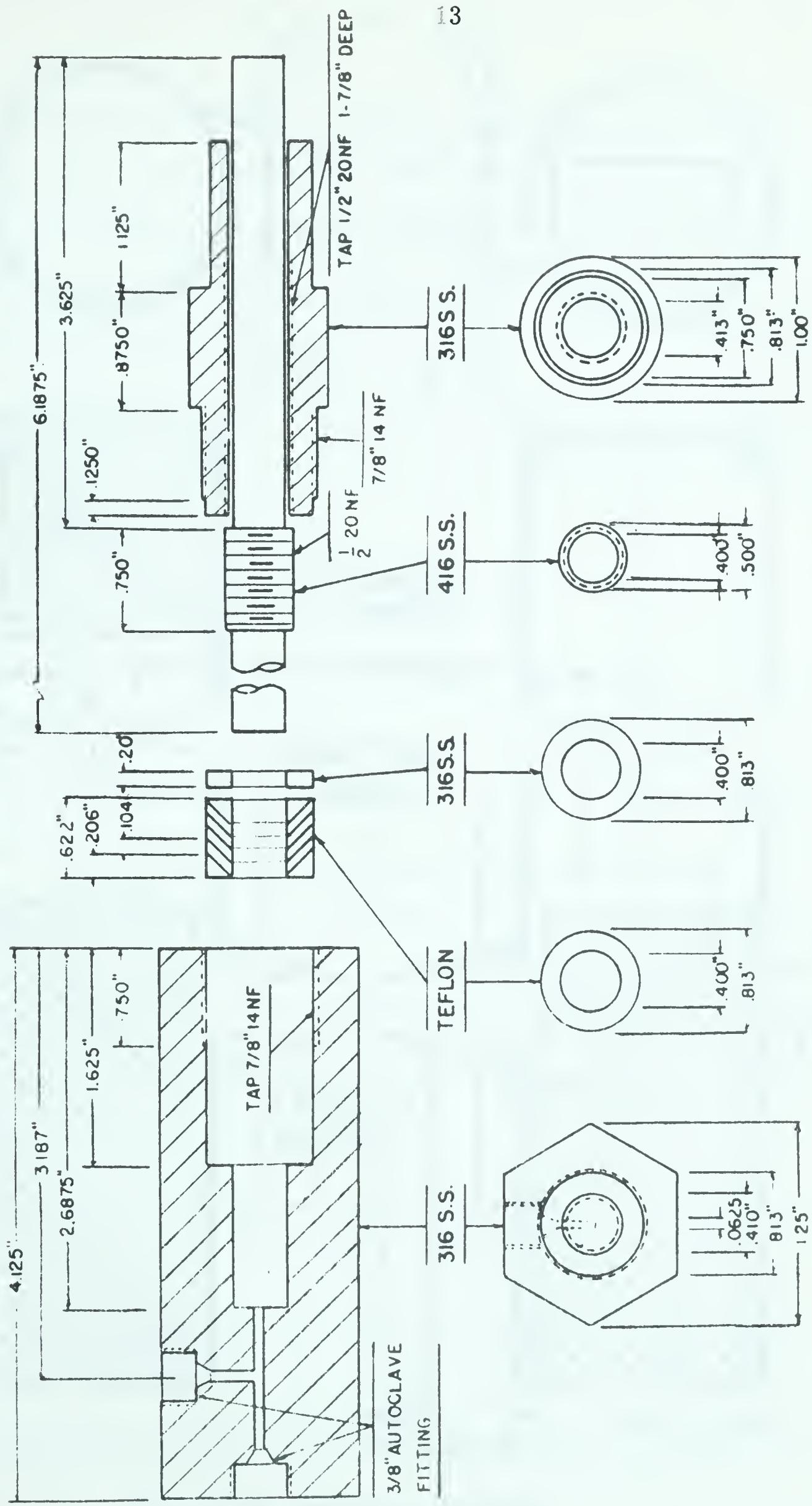


Figure #2 Micrometer Sample Pump Details



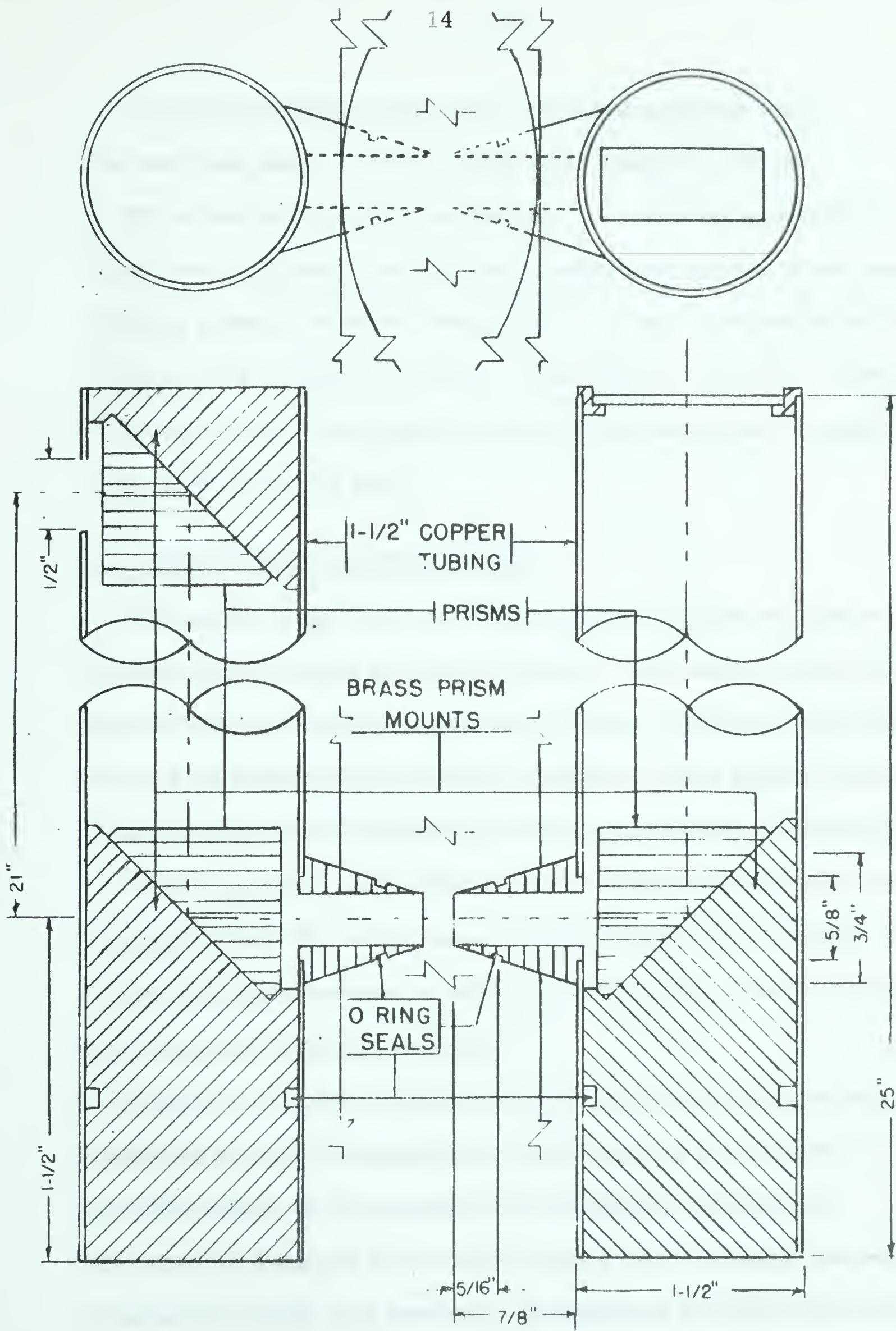


Figure #3 Periscope Details



The pressure of the system was measured using two Heise bourdon tube gauges. These gauges had ratings of 1,000 and 5,000 psi and were marked in intervals of 2 and 10 psi respectively. They were calibrated to within plus or minus one quarter of one scale division giving an expected accuracy of 0.5 psi for pressures below 1,000 psi and 3 psi for pressures from 1,000 to 5,000 psi. A constant correction factor was applied for the mercury head from the gauge zero level to the cell level.

## 2. EXPERIMENTAL PROCEDURES

The sample pump was used to inject liquid hydrogen sulphide or normal butane into the cell until a mixture of the desired composition was obtained. No attempt was made to obtain a specific composition, instead the attempt was to obtain a two phase fluid at a given pressure. A detailed description of these operations is presented in Appendix II.

The temperature and pressure of the cell were recorded and mercury injected through the bottom valve until equilibrium was obtained. This could be noted as the point at which further spraying of mercury caused no subsequent change in pressure.

Samples of the gas or liquid were then removed through the sample pump and expanded to atmospheric conditions in a gas burette. A stepwise outline of this procedure is presented in Appendix III. Considerable care had to be taken to insure that the sample line was completely purged with mercury. To minimize the chance for error



from that source the valve separating the sample pump from the cell was placed as close to the cell as possible. Duplicate samples were often taken to check the purging of the line.

When the sample was being removed mercury was added to the cell at the same volumetric rate. This prevented any disturbance of equilibrium by maintaining the system pressure.

This equipment also makes it possible to obtain vapour - liquid data by making dew point and bubble point measurements. The dew point was noted by the first appearance of liquid. This point could then be checked by reversing the procedure and noting the disappearance of the liquid. The bubble point could not be observed but could be obtained by plotting the sample volume versus the pressure. This procedure was not used except as a check. Near the critical conditions, neither the dew point nor the bubble point was apparent, and the time required to obtain each data point was longer than for the phase analysis.

### 3. MATERIAL

The volume and pressure of the cell contents were adjusted by the addition or removal of mercury. Since the combination of mercury and hydrogen sulphide, in the presence of any impurity, such as water, caused nearly immediate blackening of the mercury, considerable care was taken to insure that pure mercury was used. Initially, dirty mercury was paper filtered or decanted to remove any surface dirt. It was then purified in an Oxifier manufactured by the Bethlehem



Instrument Company and refiltered. A fine spray of this partially cleaned mercury was then allowed to fall through a series of washing columns. The columns, containing benzene, dilute nitric acid, and distilled water, washed any remaining oils or dust from the mercury. A triple distillation under vacuum was the final step in the mercury preparation.

The two fluids, normal butane and hydrogen sulphide, had to be purified and dried. Initially, the normal butane was purified in a Podbielniak Low Temperature Distillation Apparatus using a reflux ratio sufficiently high to remove any iso-butane. The purified butane could then be shown to have less than 0.1 mole percent iso-butane but would contain considerable air. This air was removed by freezing the butane with liquid air and evacuating the air from the sample cylinder.

Since the maximum product obtained from each run by the above procedure would be nine millilitres of liquid butane, it was too time consuming. As a result, a distillation column was built to operate at pressures above atmospheric with much larger volumes of butane. This column, built from 30 feet of 3/4 inch copper pipe, was packed with activated silica beads. The butane obtained from the column was then purified by freezing and evacuation until no air was indicated by chromatographic analysis. The resulting normal butane could be shown to be at least 99.9 mole percent pure.

Similarly, the hydrogen sulphide was also initially purified on the Podbielniak column. However, because of the danger involved and the



extreme difficulty of separating any carbon dioxide, the procedure was abandoned in favour of two driers. The first was filled with anhydrous calcium chloride, and the second with calcium sulphate. After freezing and evacuating, the product was at least 99.9 mole percent pure. The only impurity was a trace of carbon dioxide.

#### 4. ANALYSIS

A Burrel K-2 "Kromo-Tog" was used to analyse the samples both as pure samples and as mixtures taken from the cell. The column conditions were:

Column	: Tricresylphosphate on celite (30/70)
Column size	: 25 feet of 1/4 " aluminum tubing
Carrier gas	: Helium at 35 ml./50 secs.
Detector current	: 180 ma.
Column temperature	: 90° F.
Sample size	: 1 millilitre

The column temperature was maintained by means of a thermostated water bath. At the conditions stipulated, the normal butane and the hydrogen sulphide were not completely separated. However, a satisfactory calibration was obtained by measuring peak heights for various mixtures and plotting a curve through the resulting points. The calibration curve so obtained is presented as Figure 4.

The column was shown to separate the following compounds clearly in small amounts; methane or air, carbon dioxide, propane, iso-butane,



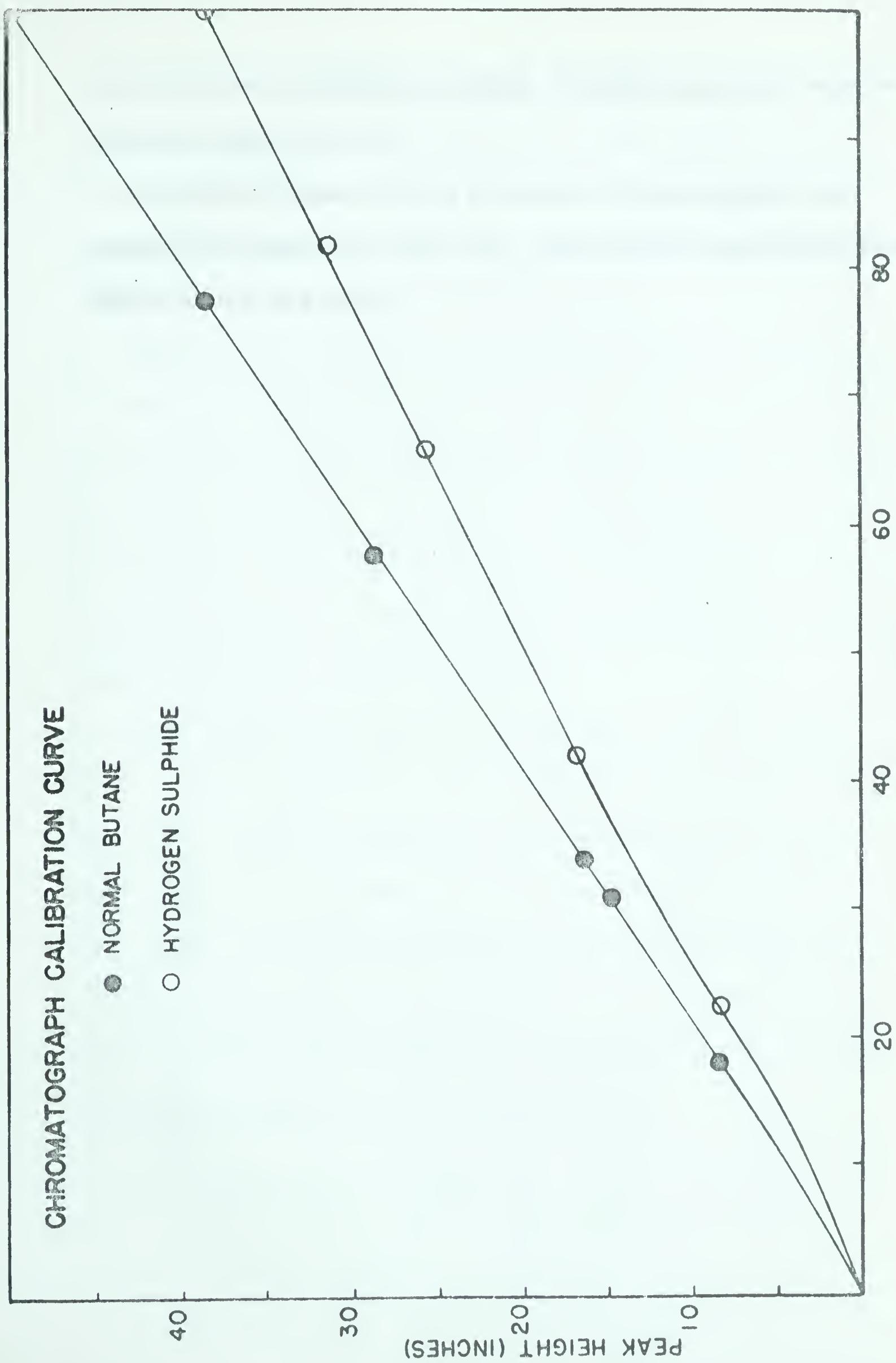


Figure #4 Calibration of Chromatograph for Hydrogen Sulphide - Normal Butane Mixtures



normal butane and hydrogen sulphide. Heavier components were not present in these mixtures.

A separate column, used on a Beckman Chromatograph, was employed to analyse for water (17). This analysis indicated the samples did not contain any water.



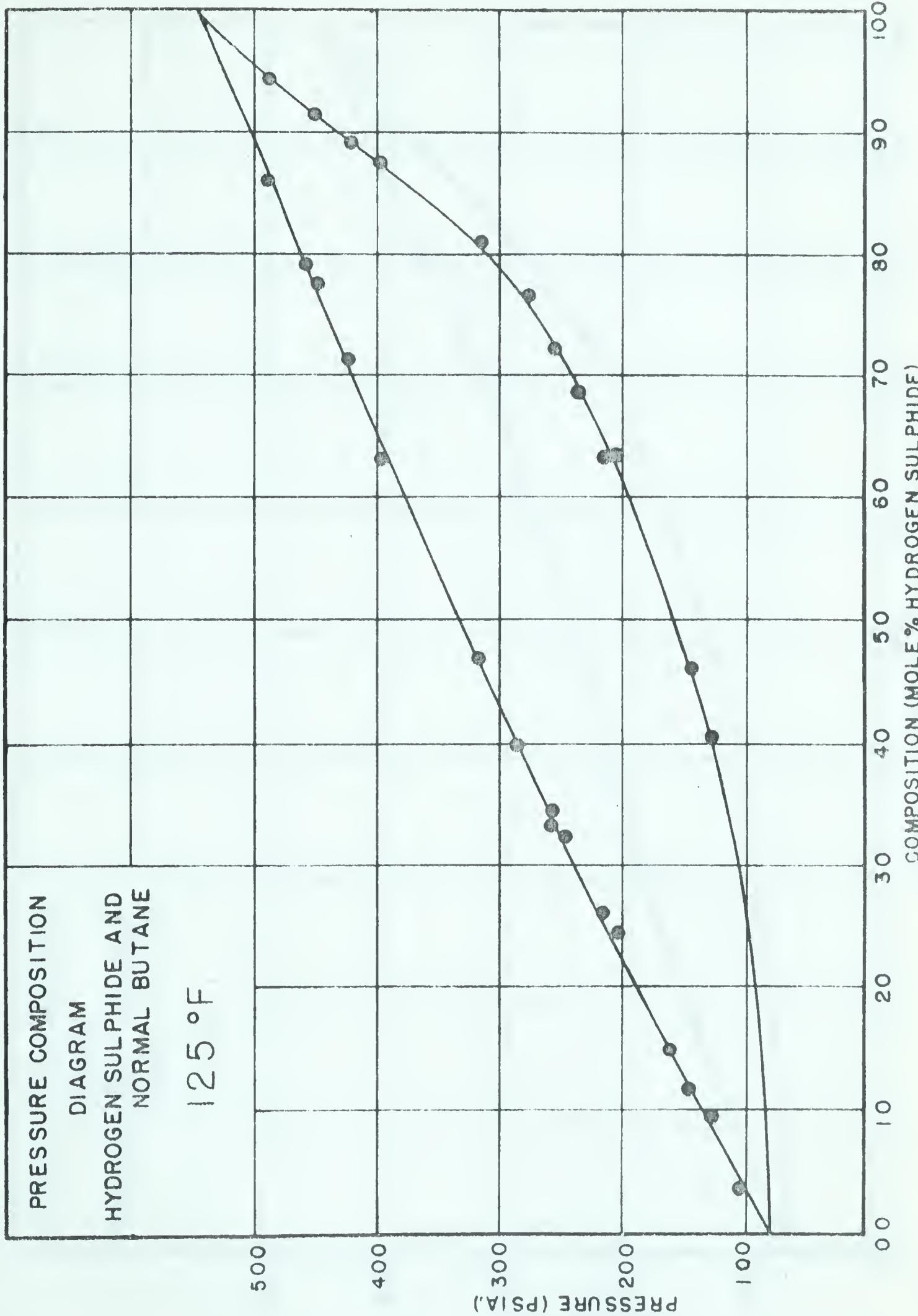
#### D. EXPERIMENTAL RESULTS

To gain experience in the handling of the cell, the first series of data was obtained at a temperature of  $125^{\circ}\text{F}.$ , that is,  $25^{\circ}$  above that presented by Sandercock (35). The results of this run are shown in Table 1 of Appendix I and plotted on Figure 5.

This practice run showed the experimental technique was satisfactory. It indicated that equilibrium could be obtained in about two hours and that the pressure should be increased between readings. If the sample was nearly all liquid the pressure was increased by the addition of hydrogen sulphide. If the sample was mostly gas, mercury was added to increase the pressure. It was found that five mixtures would define a phase envelope for a specific temperature.

Further data were obtained at temperatures of  $175^{\circ}\text{F}.$ ,  $200^{\circ}\text{F}.$ ,  $225^{\circ}\text{F}.$ ,  $250^{\circ}\text{F}.$ , and  $275^{\circ}\text{F}.$ . These results are presented in Tables II, III, IV, V and VI of Appendix I and on Figures 6, 7, 8, 9 and 10. Two composite P-T-X diagrams were drawn from the smoothed data, Figure 11 with the temperature as the parameter and Figure 12 with the composition as the parameter. These diagrams also show the critical locus of the system. The experimental data were consistent and could be quite readily duplicated.





Figure#5 The Vapour - Liquid Behavior of the Binary System Hydrogen Sulphide - Normal Butane @ 125 F.



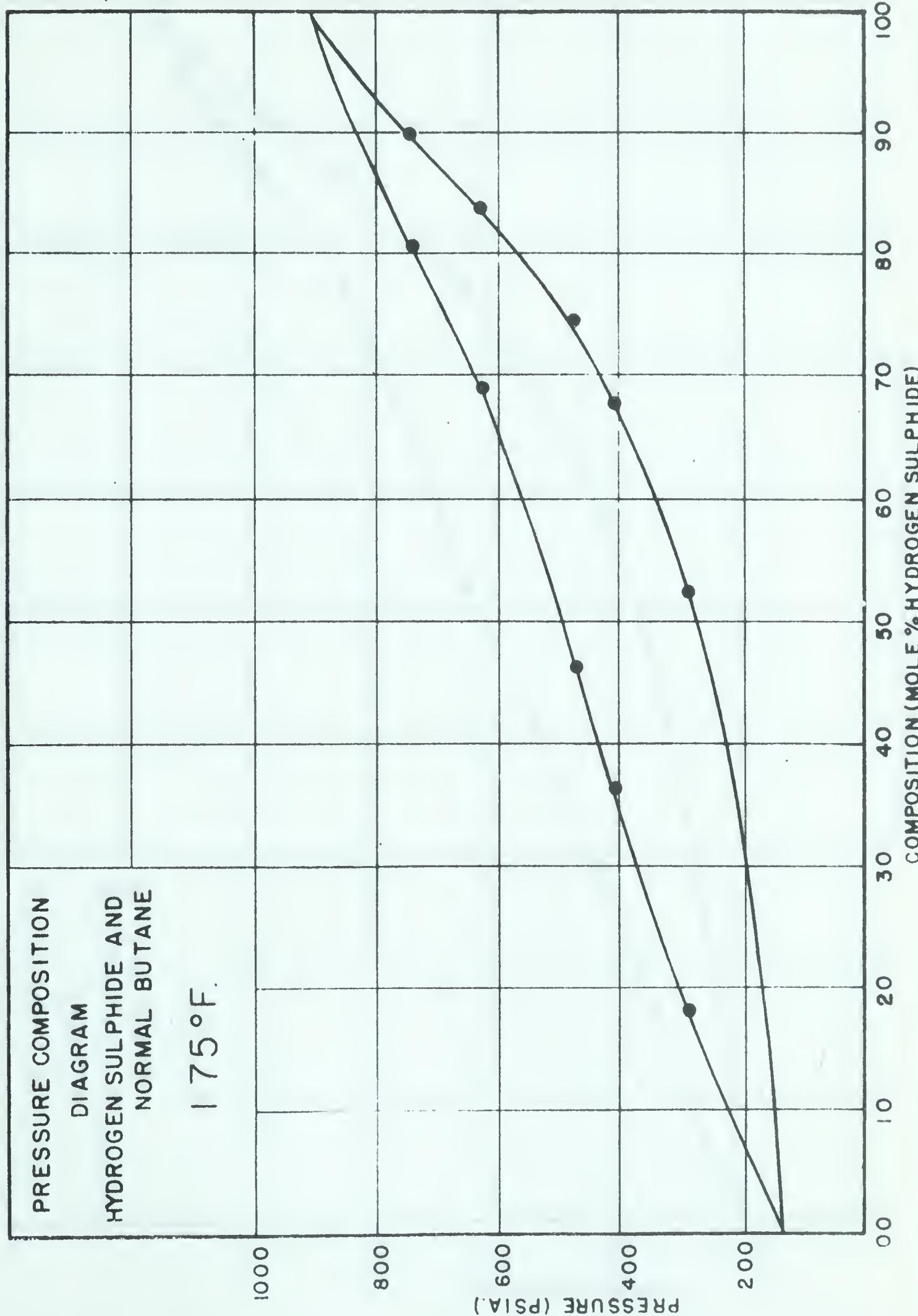
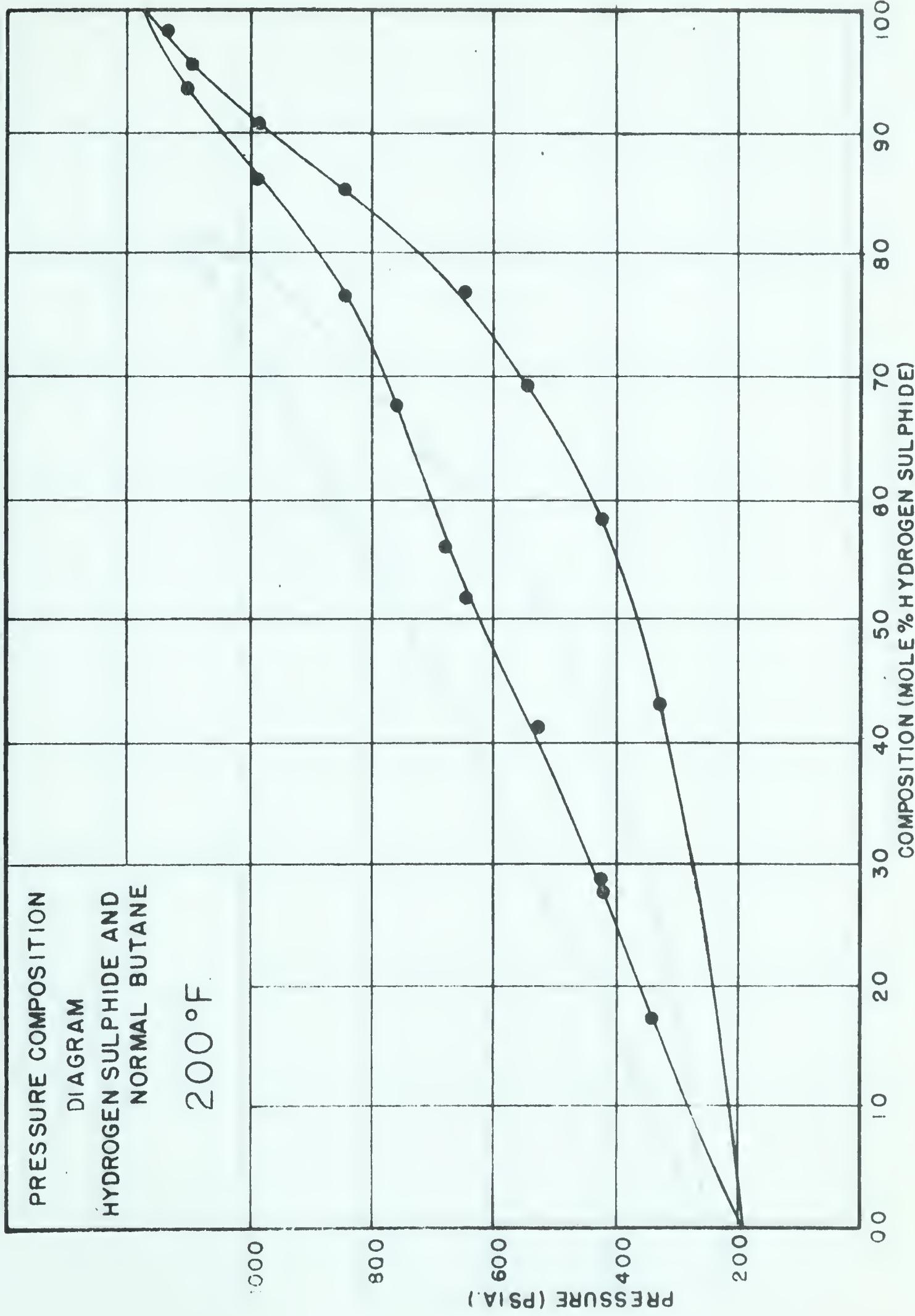


Figure #6 The Vapour -Liquid Behavior of the Binary System Hydrogen Sulphide - Normal Butane @ 175 F.





Figure#7 The Vapour - Liquid Behavior of the Binary System Hydrogen Sulphide - Normal Butane @ 200 F.



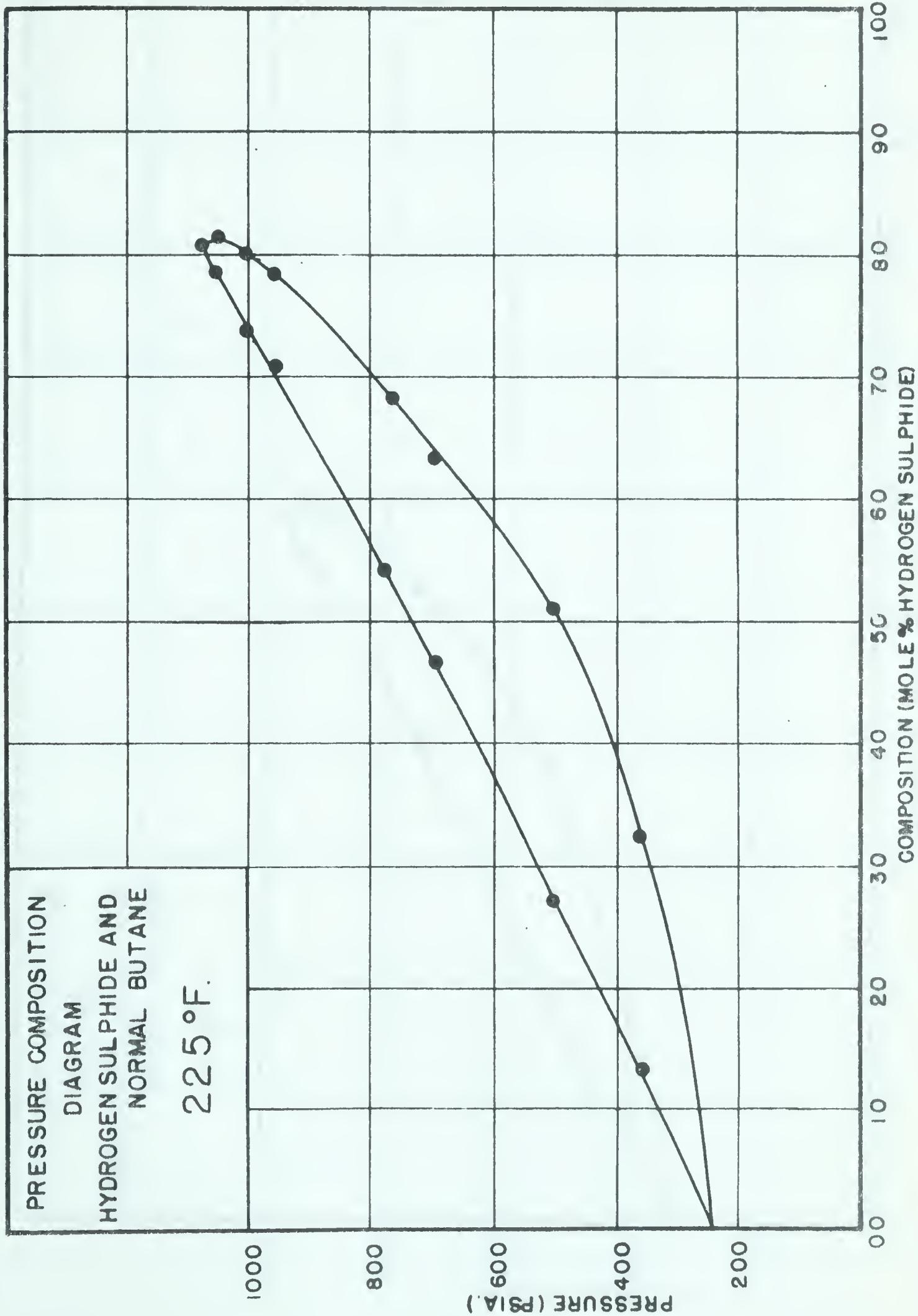


Figure #8 The Vapour - Liquid Behavior of the Binary System Hydrogen Sulphide and Normal Butane @225 F.



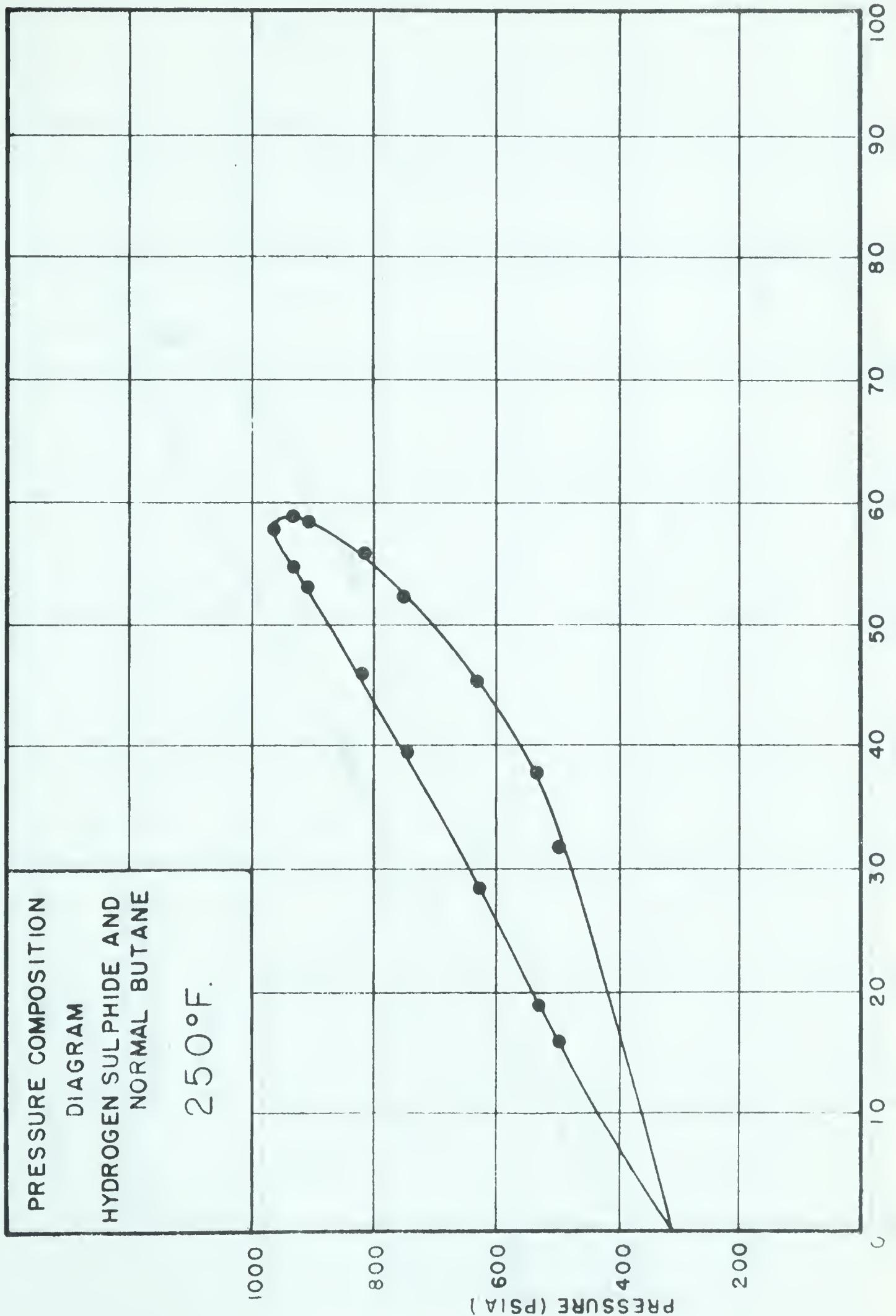


Figure #9 The Vapour - Liquid Behavior of the Binary System Hydrogen Sulphide - Normal Butane @250 F.



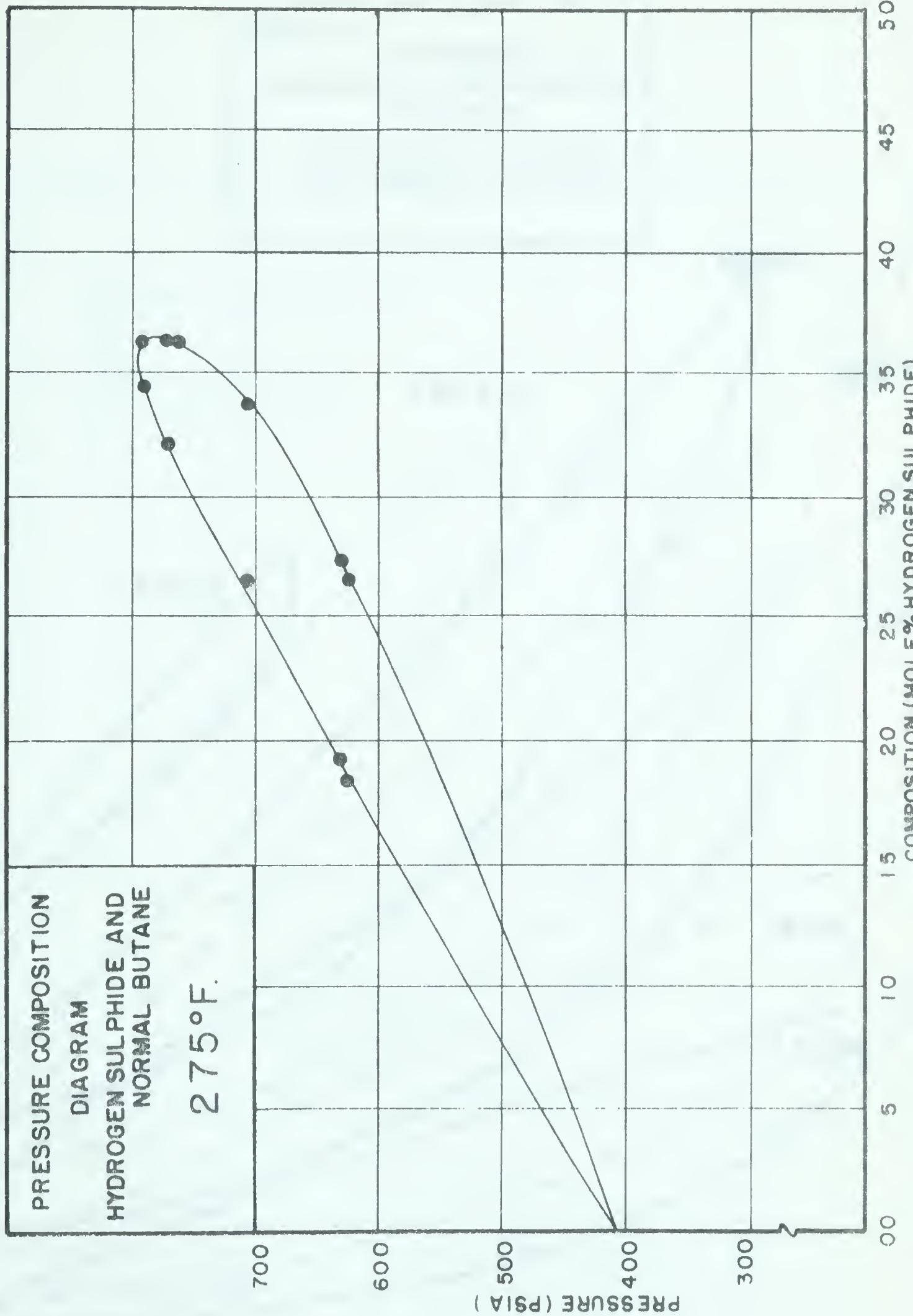
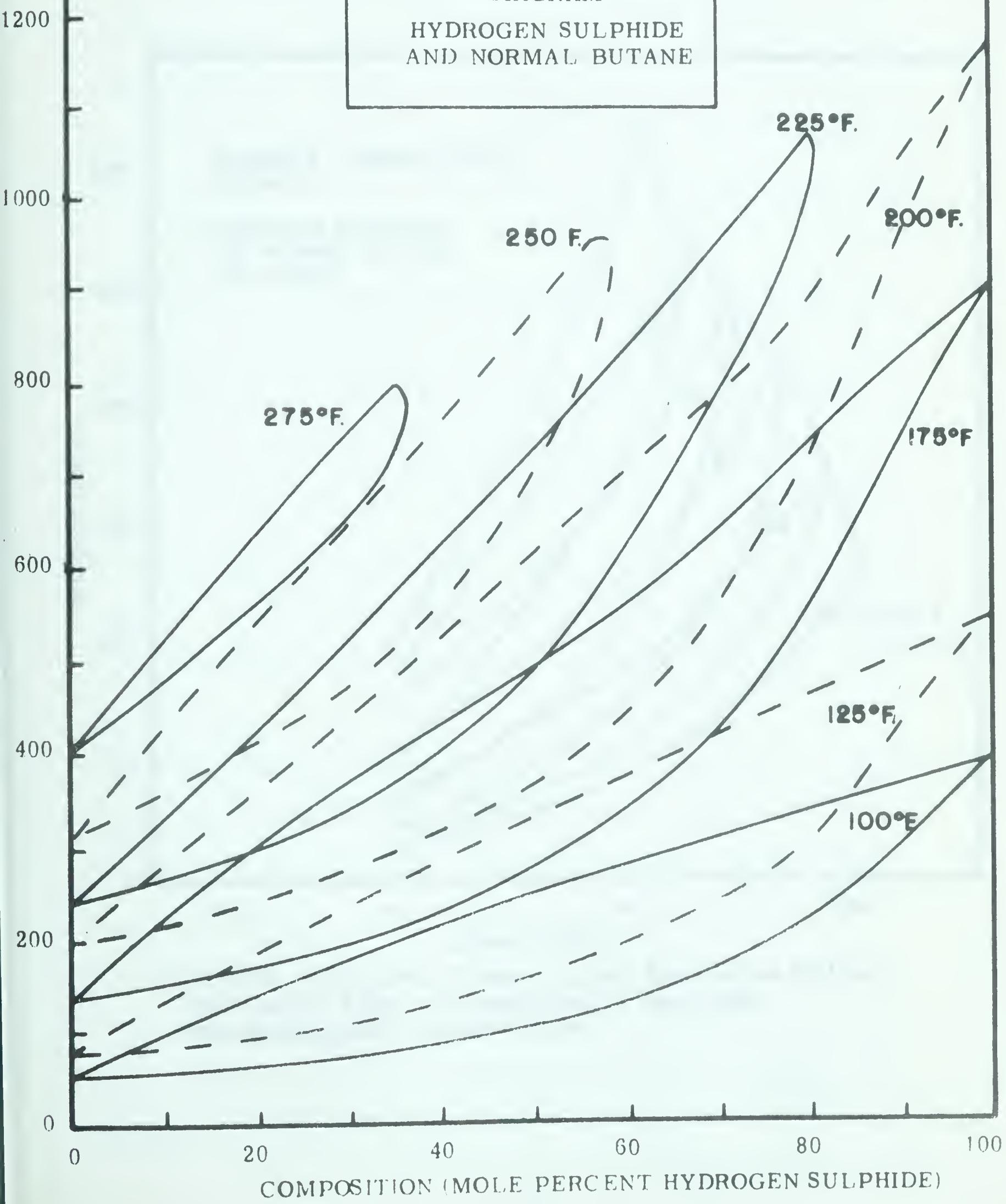


Figure #10 The Vapour - Liquid Behavior of the Binary System Hydrogen Sulphide - Normal Butane @ 275 F.



Figure #11  
COMPOSITE  
PRESSURE - COMPOSITION  
DIAGRAM  
HYDROGEN SULPHIDE  
AND NORMAL BUTANE





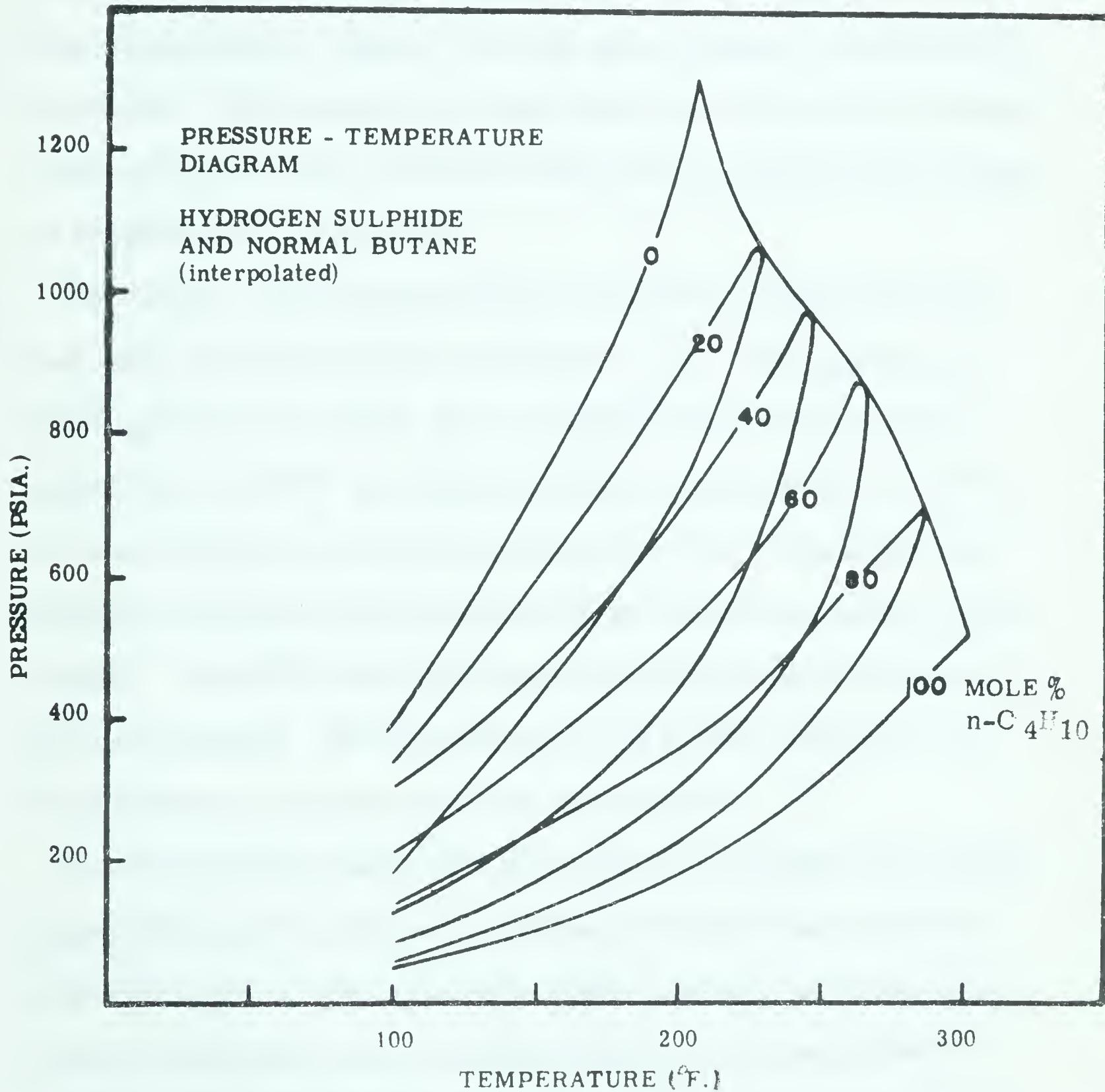


Figure #12 A Composite Vapour - Liquid Equilibrium Diagram  
 Indicating the Effect of Composition for the System  
 Hydrogen Sulphide - Normal Butane



## E. DISCUSSION

The results indicate an azeotrope was not formed at any composition or temperature for the vapor - liquid equilibrium of hydrogen sulphide and normal butane. However, the data did not indicate a typical binary behaviour. The deviation from ideal laws such as Raoult's and Dalton's laws was considerable and varied from positive to negative with changes in temperature or composition.

The vapour - liquid equilibrium for the system at each temperature was calculated using Raoult's and Dalton's laws. The experimental bubble point line for 100<sup>o</sup>F. was at a higher pressure than the ideal calculation, at 125<sup>o</sup>F. the deviation was not as pronounced. At 175<sup>o</sup>F. the experimental data indicated a value lower than the ideal for high hydrogen sulphide concentrations and above the ideal for lower concentrations. At 200<sup>o</sup>F. the bubble point line remained below the ideal for all concentrations. As the temperature was further increased, the ideal prediction remained above the experimental.

The dew point line was always above the ideal and exhibited a typical binary behaviour for mixtures containing less than 75 mole percent hydrogen sulphide. For mixtures of higher hydrogen sulphide concentration the dew point curve reversed curvature at temperatures of 125<sup>o</sup>F., 175<sup>o</sup>F., and 200<sup>o</sup>F.

The combination of the dew point and bubble point curves indicated a marked tendency toward an azeotrope even though an azeotrope did not exist.



The equilibrium ratios were calculated from the smoothed experimental data and plotted on Figures 13 - 24 inclusive. On these plots the experimental data are compared with those obtained by various authors for the methane, ethane, propane and normal pentane - hydrogen sulphide binaries. The ratios plotted for hydrogen sulphide on Figures 13 - 18 are also compared with those presented in NGSMA (19) for a convergence pressure of 1000 psia. This convergence pressure was the only value presented in the NGSMA databook. However, since the expected range of critical pressures was from 550 psia. to 1,400 psia., the value of 1,000 psia. for the convergence pressure should not give unreasonable results. The ratios plotted for the hydrocarbon components on Figures 19 - 24 are compared with the general equilibrium ratios presented in NGSMA for normal butane in systems having convergence pressures of 800 and 1,000 psia. These values were chosen as the most descriptive values for any normal butane - hydrogen sulphide system.

At 125°F. the equilibrium ratios plotted on Figure 13 showed the hydrogen sulphide ratios for the normal butane binary crossing the NGSMA and the propane binary ratios but converging with those presented for the normal pentane binary at a pressure of 500 psia. It was apparent that a convergence pressure of less than 1,000 psia. would be more applicable.

As shown in Figure 14, the normal butane binary data at 175°F. gave equilibrium ratios that crossed the NGSMA and pentane binary



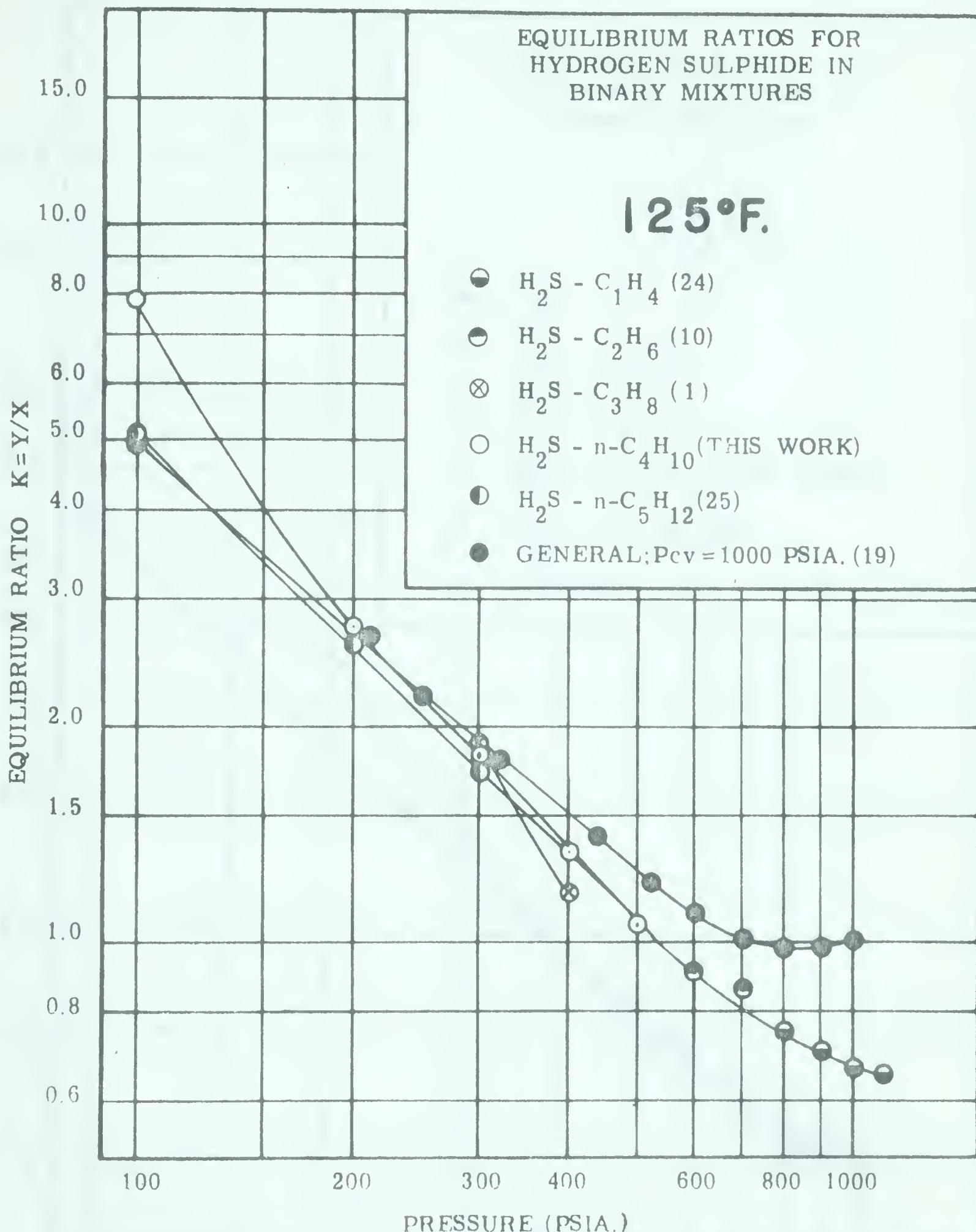


Figure #13 A Comparison of Equilibrium Ratios for Hydrogen Sulphide in Various Binary Systems at 125 F. with Those Presented in NGSMA for a Convergence Pressure of 1000 psia.



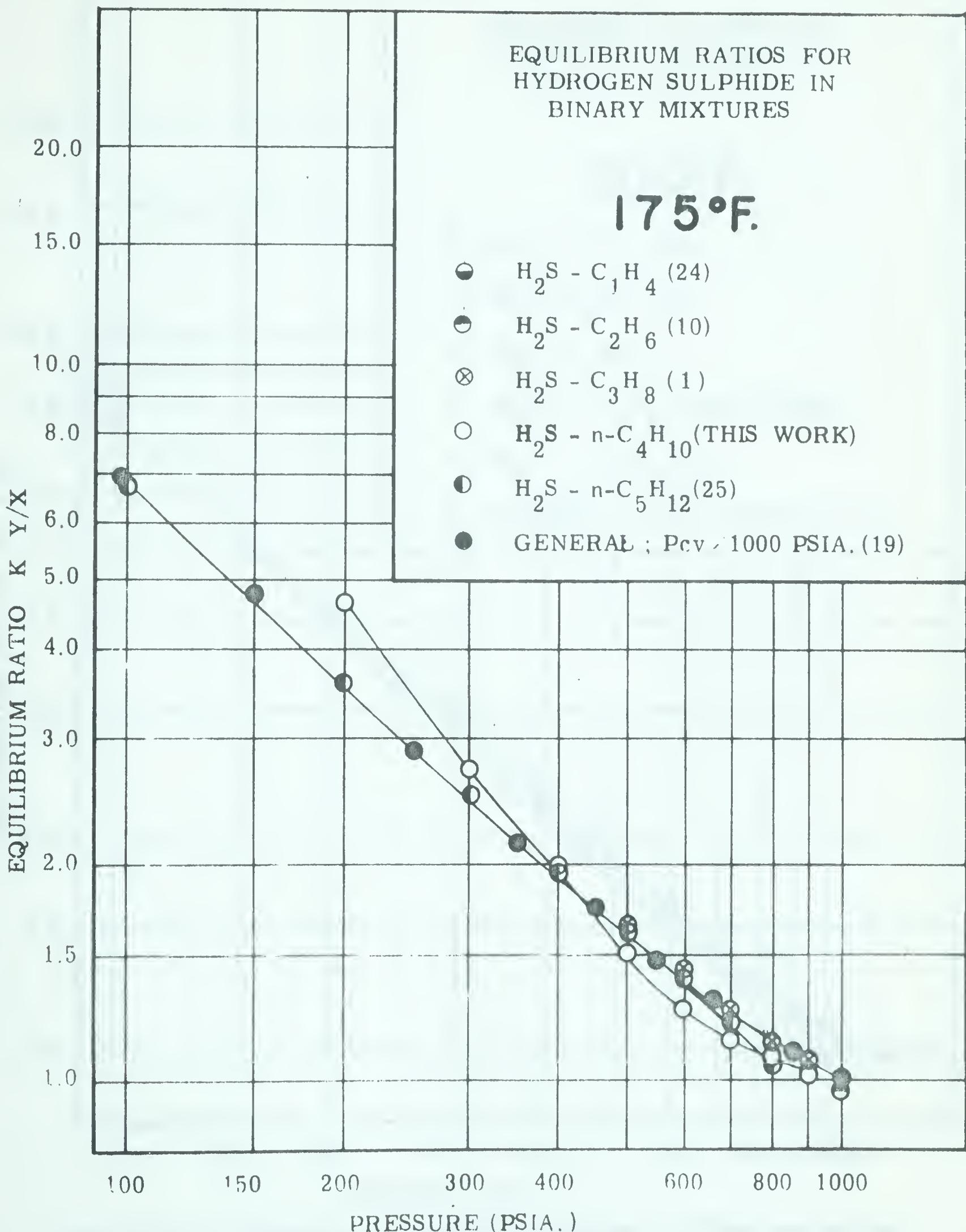


Figure #14 A Comparison of Equilibrium Ratios for Hydrogen Sulphide in Various Binary Systems at 175 F. with Those Presented in NGSMA for a Convergence Pressure of 1000psia.



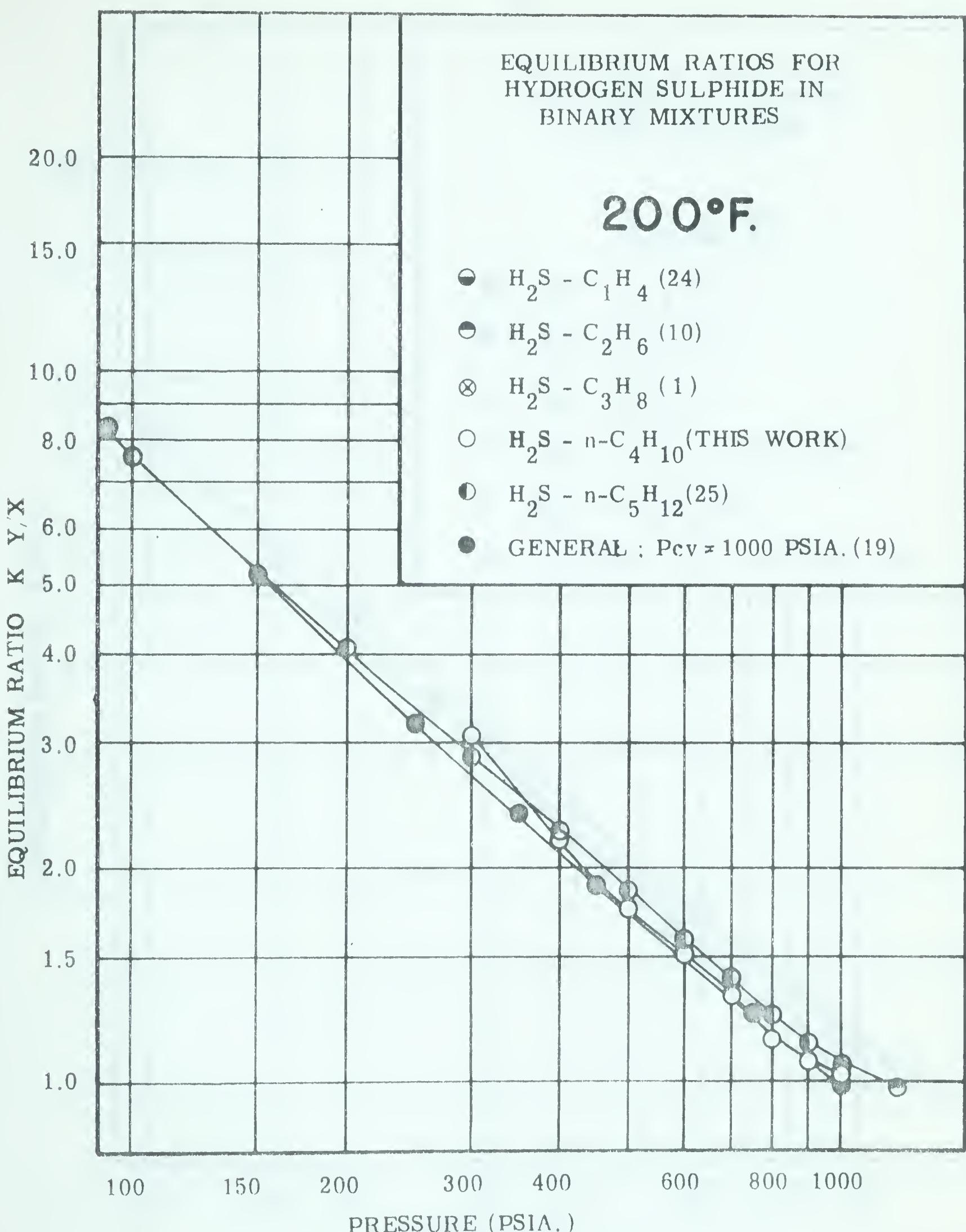


Figure #15 A Comparison of Equilibrium Ratios for Hydrogen Sulphide in Various Binary Systems at 200 F. with Those Presented in NGSMA for a Convergence Pressure of 1000 psia.



EQUILIBRIUM RATIOS FOR  
HYDROGEN SULPHIDE IN  
BINARY MIXTURES

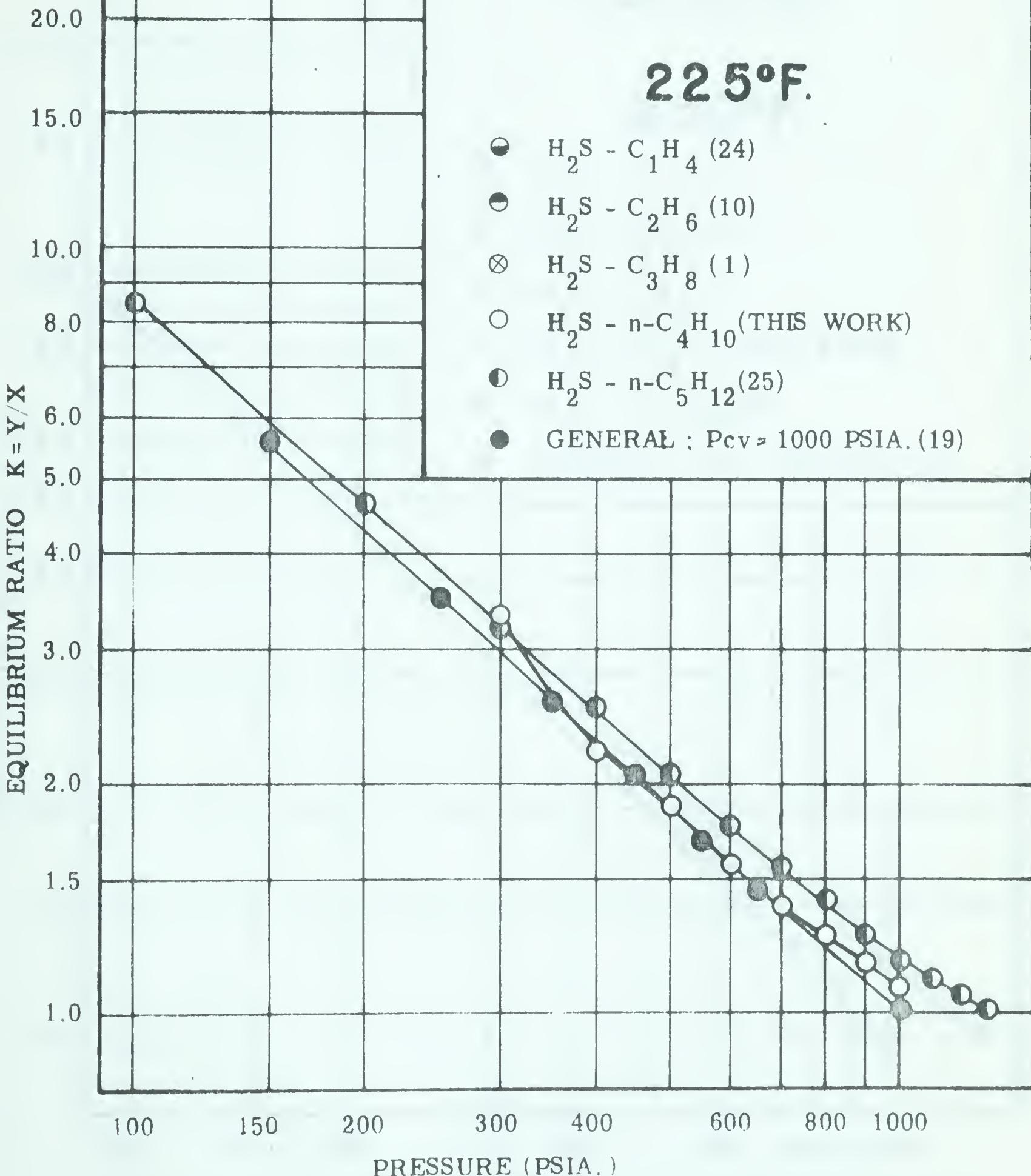


Figure #16 A Comparison of Equilibrium Ratios for Hydrogen Sulphide in Various Binary Systems at 225 F. with Those Presented in NGSMA for a Convergence Pressure of 1000 psia.



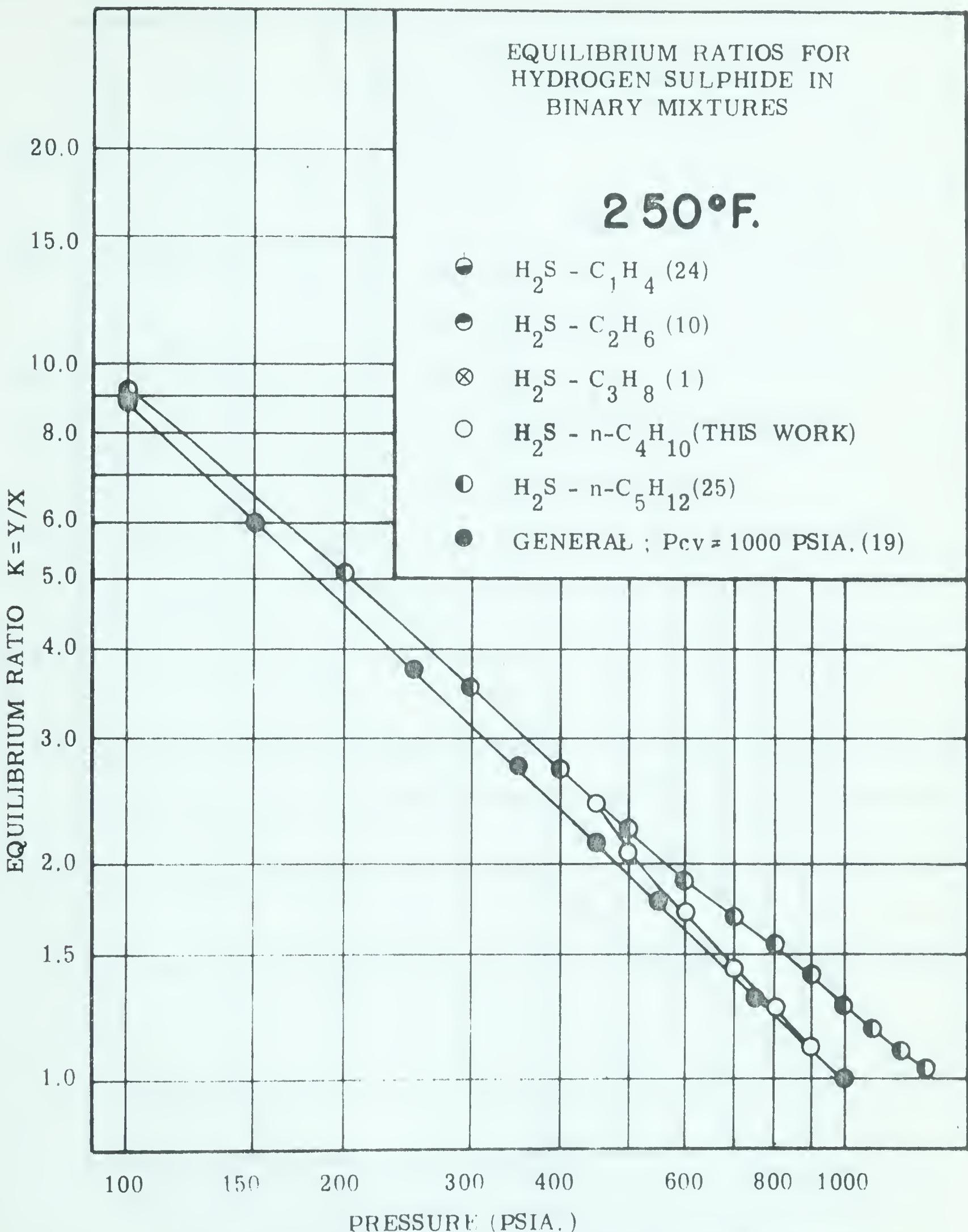


Figure #17 A Comparison of Equilibrium Ratios for Hydrogen Sulphide in Various Binary Systems at 250 F. with Those Presented in NGSMA for a Convergence Pressure of 1000 psia.



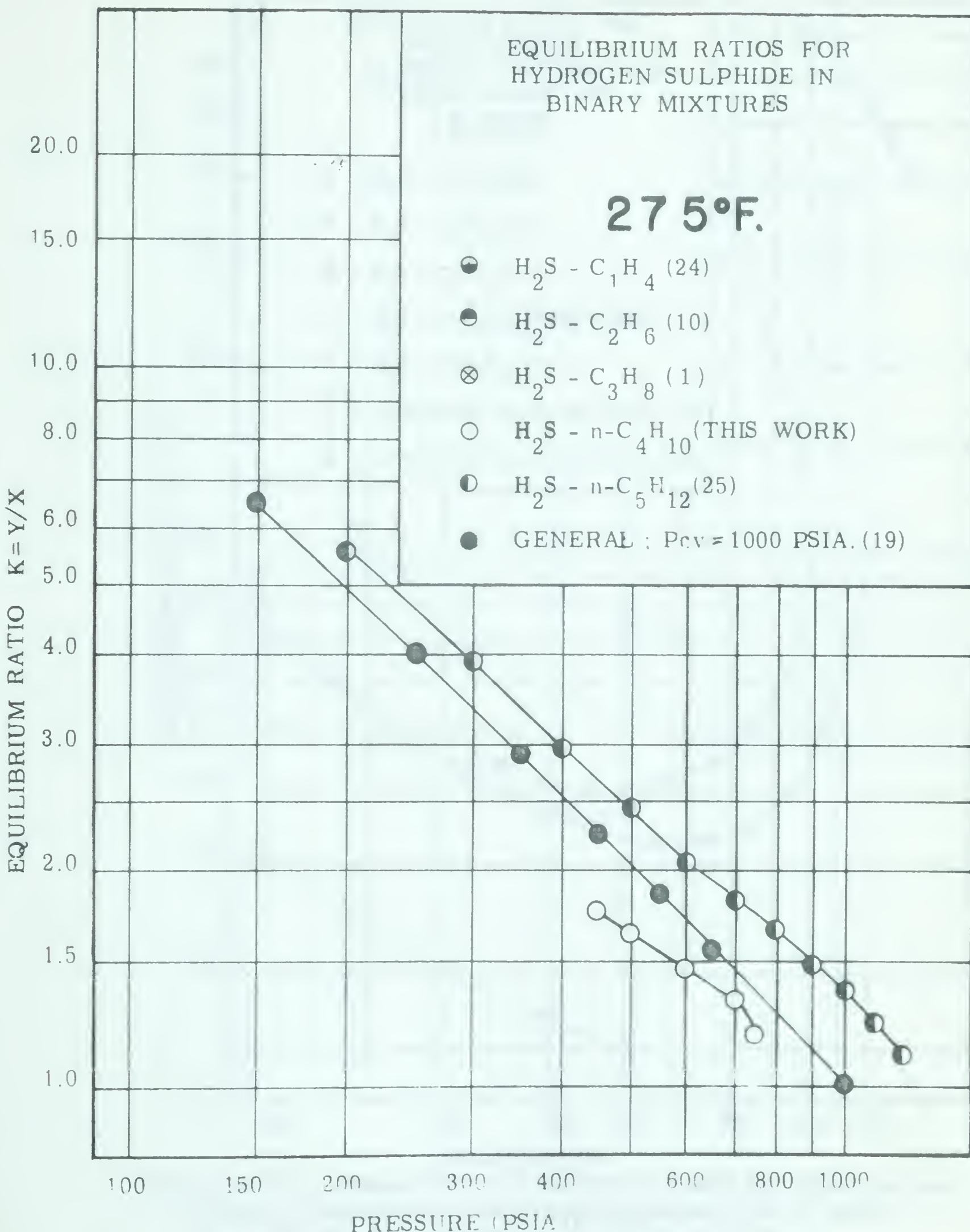


Figure #18 A Comparison of Equilibrium Ratios for Hydrogen Sulphide in Various Binary Systems at 275 F. with Those Presented in NGSMA for a Convergence Pressure of 1000 psia.



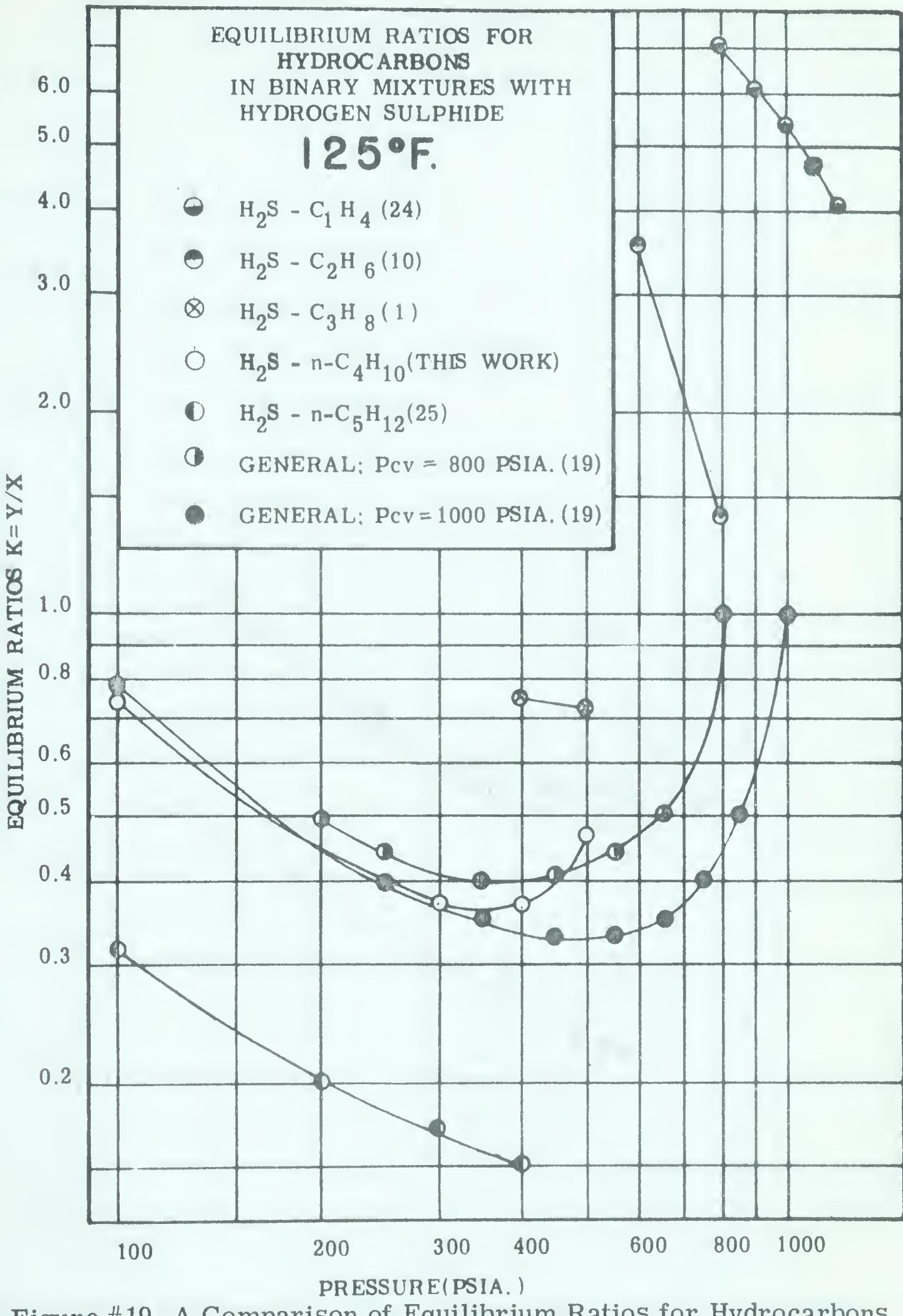


Figure #19 A Comparison of Equilibrium Ratios for Hydrocarbons in Binary Mixtures with Hydrogen Sulphide at 125 F. with Those Obtained From NGSMA for n-Butane at Two Convergence Pressures.



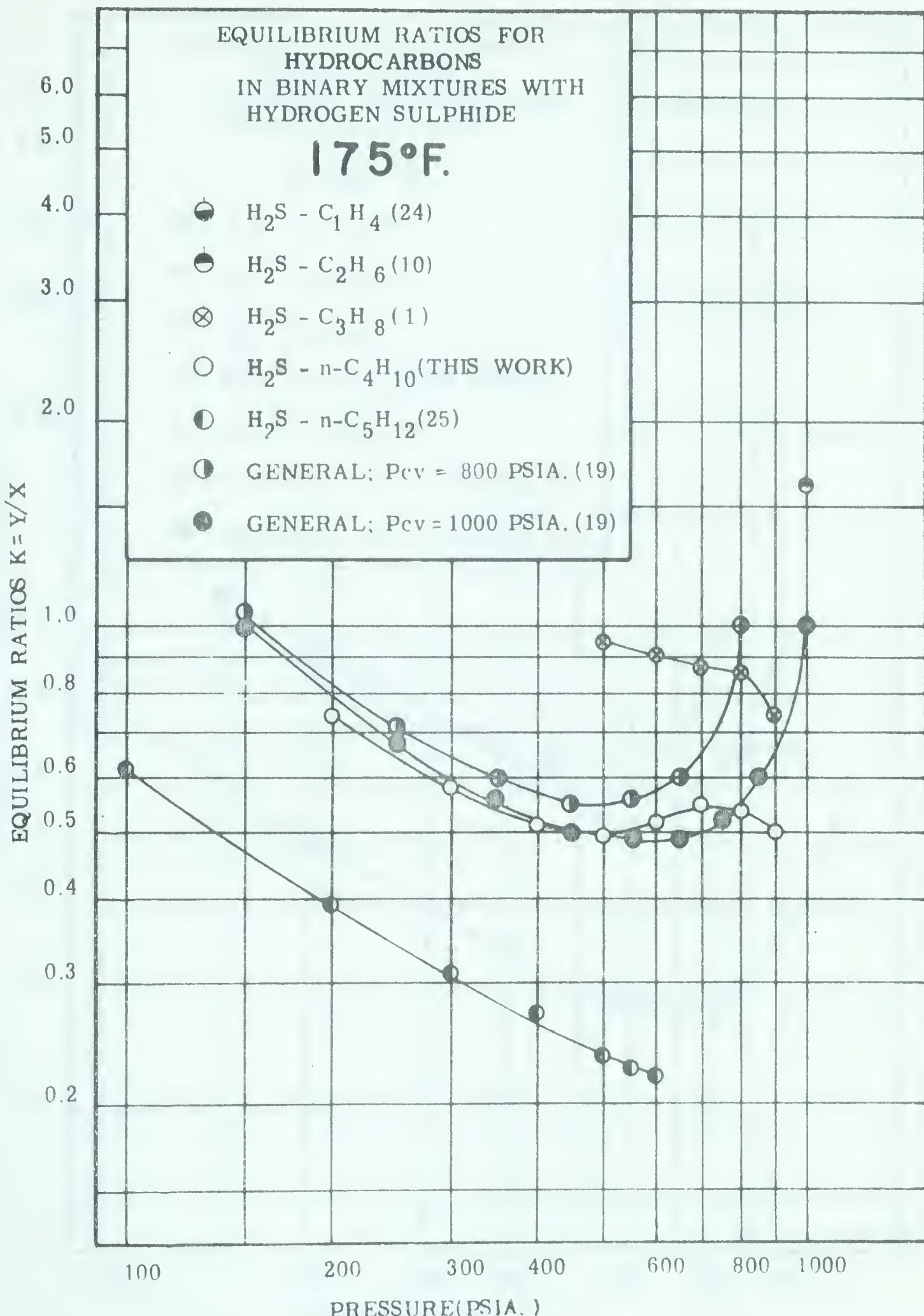


Figure #20 A Comparison of Equilibrium Ratios for Hydrocarbons in Binary Mixtures with Hydrogen Sulphide at 175 F. with Those Obtained From NGSMA for n-Butane at Two Convergence Pressures.



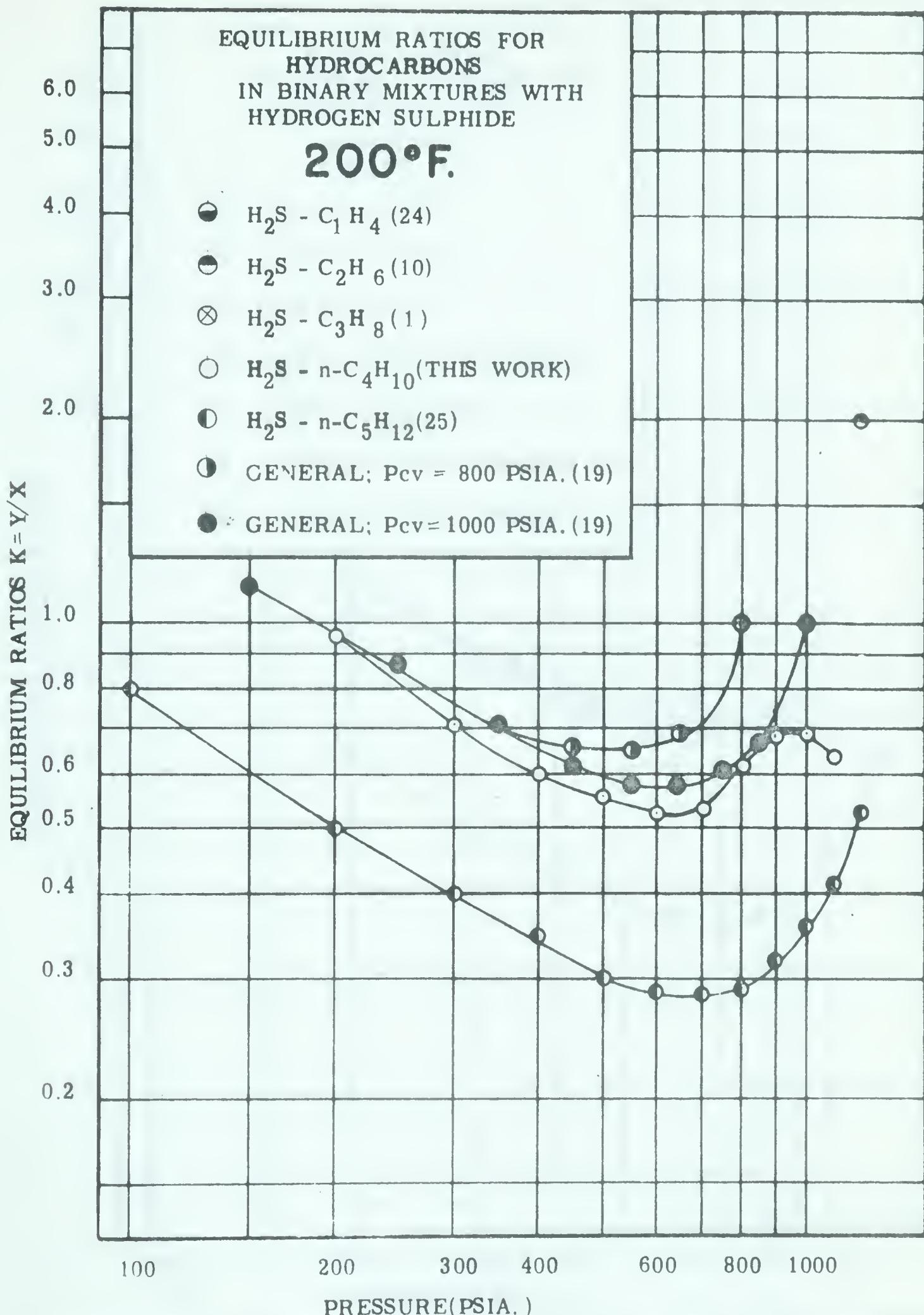


Figure #21 A Comparison of Equilibrium Ratios for Hydrocarbons in Binary Mixtures with Hydrogen Sulphide at 200 F. with Those Obtained From NGSMA for n-Butane at Two Convergence Pressures.



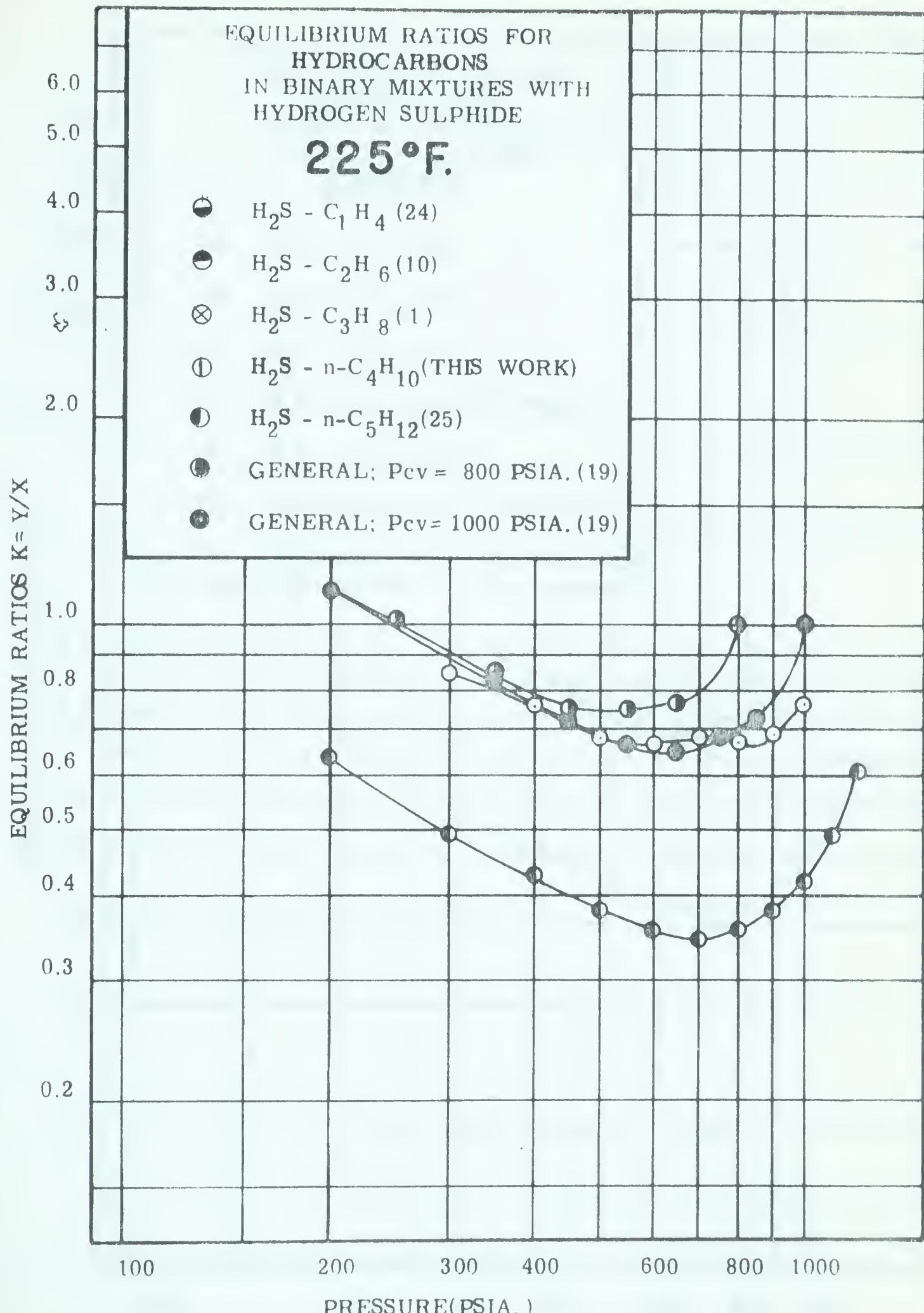


Figure #22 A Comparison of Equilibrium Ratios for Hydrocarbons in Binary Mixtures with Hydrogen Sulphide at 225 F. with Those Obtained From NGSMA for n-Butane at Two Convergence Pressures.



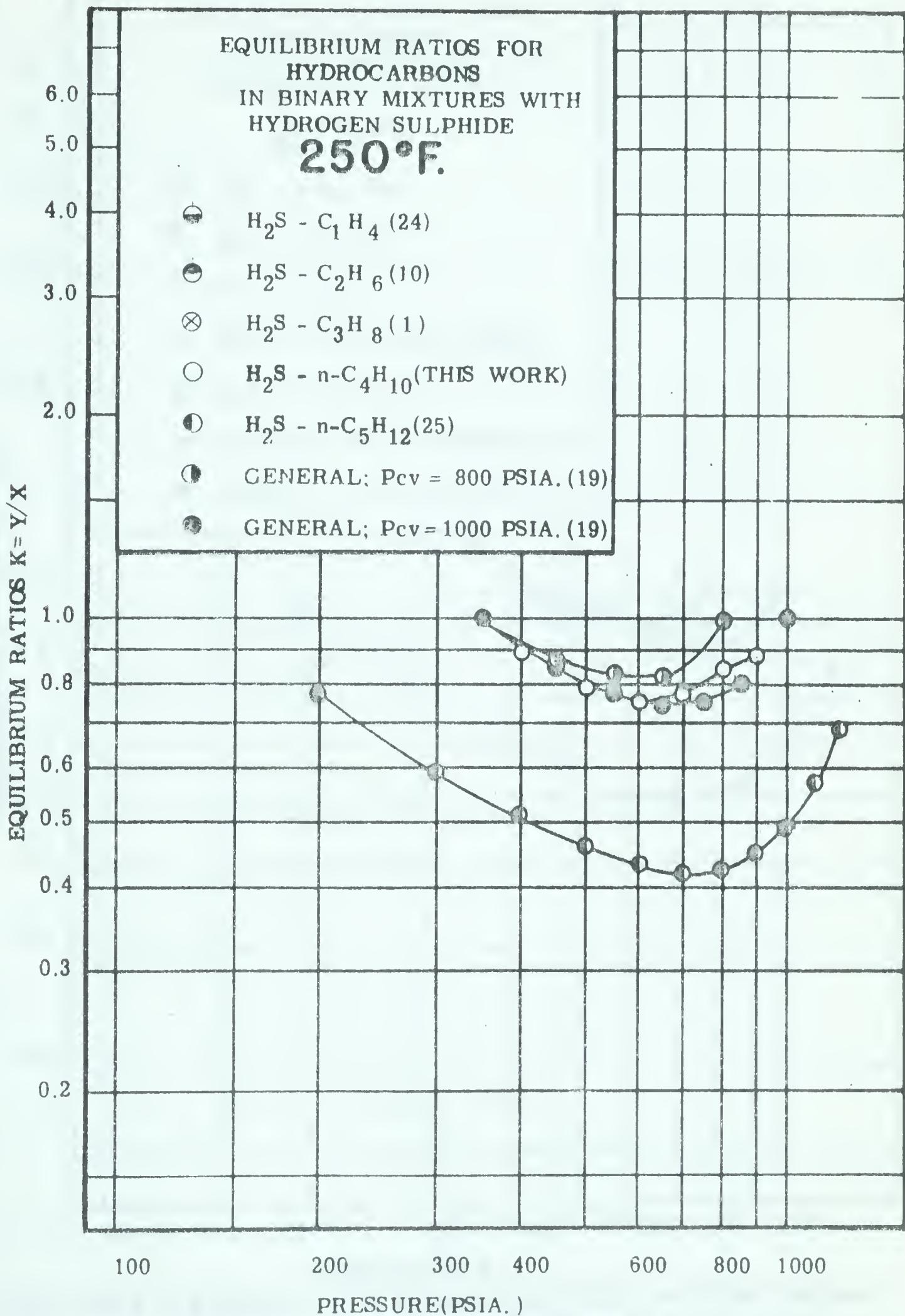


Figure #23 A Comparison of Equilibrium Ratios for Hydrocarbons in Binary Mixtures with Hydrogen Sulphide at 250 F. with Those Obtained From NGSMA for n-Butane at Two Convergence Pressures.



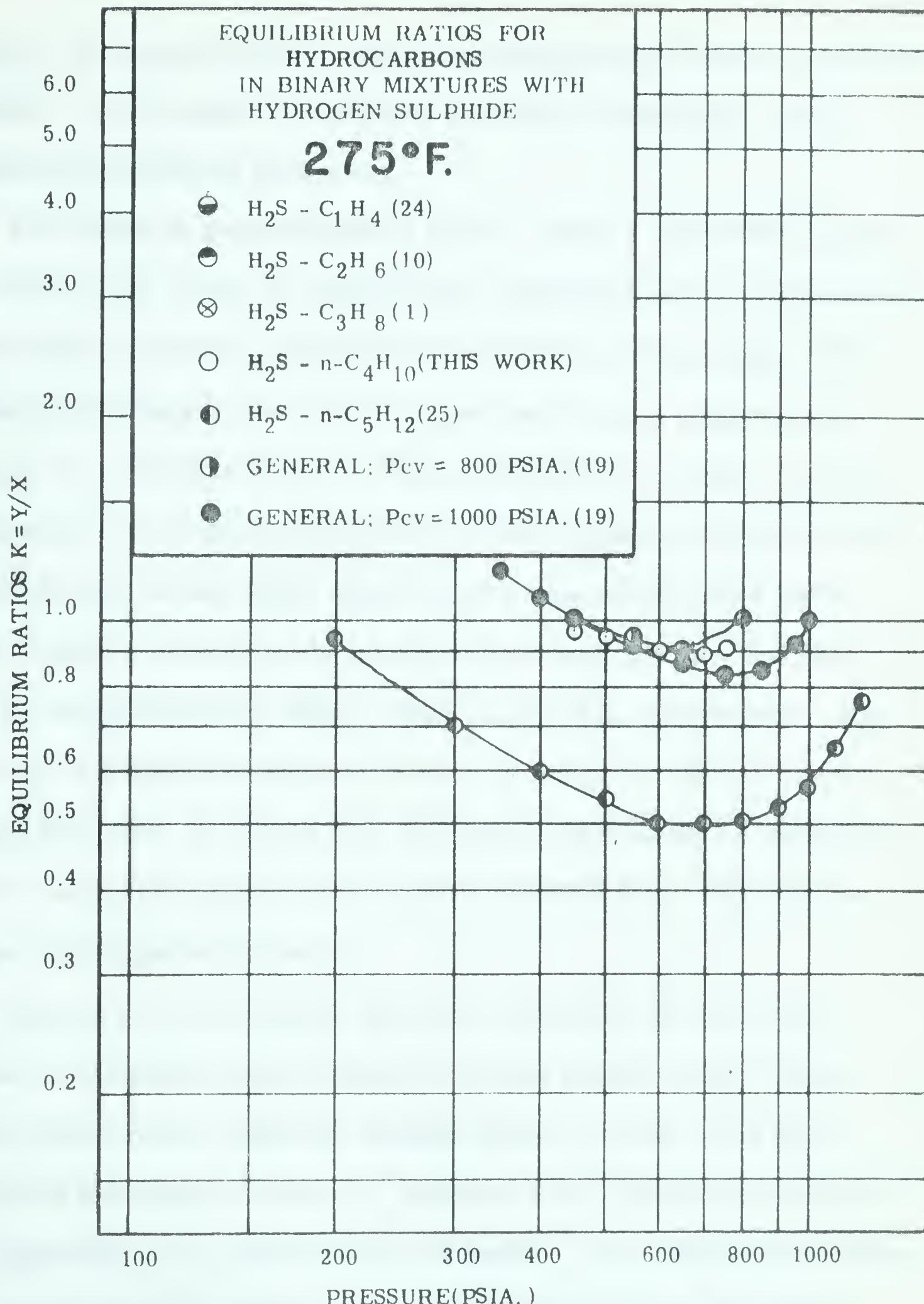


Figure #24 A Comparison of Equilibrium Ratios for Hydrocarbons in Binary Mixtures with Hydrogen Sulphide at 275 F. with Those Obtained From NGSMA for n-Butane at Two Convergence Pressures.



ratios. The propane binary ratios were larger for all values of pressure plotted. In all cases a convergence pressure of 1,000 psia. was an adequate composition parameter.

The results at temperatures of 225°F., 250°F., and 275°F., plotted on Figures 16, 17 and 18 respectively, indicated a very good agreement with those presented in NGSMA for most of the pressure range. The experimental equilibrium ratios formed broad curves apparently tangential to the NGSMA curves. When the pressure was above 500 psia., the pentane binary gave equilibrium ratios for hydrogen sulphide above those for the normal butane binary at all temperatures above 200°F. The critical pressures of the mixtures were 1180, 960 and 790 psia. for the temperatures of 225°F., 250°F. and 275°F. respectively. For a binary system the critical pressure is synonymous with the convergence pressure. In view of this, the plot of the equilibrium ratios at 275°F. would be expected to be below the NGSMA data. This was the case as is shown on Figure 18.

Figures 19 to 24 inclusive present a comparison of the normal butane equilibrium ratios, obtained in various manners, with those of other hydrocarbon - hydrogen sulphide binary systems. The first figure of this series, Figure 18, indicates a low convergence pressure is applicable at low pressures for the system. The experimental ratios for normal butane at 125°F. cross both NGSMA curves. The other binary systems show the effect of volatility on the relative value of the equilibrium ratios. The hydrocarbon equilibrium ratios for the



methane - hydrogen sulphide binary are very high. For the ethane - hydrogen sulphide binary they are slightly lower but still above 1.0. The hydrocarbon equilibrium ratios are below 1.0 for the propane - hydrogen sulphide system. The ratios are still smaller for the normal butane binary and become even smaller for the pentane - hydrogen sulphide binary.

The equilibrium ratios for 175°F. for normal butane on Figure 19 show a definite tendency toward azeotropic behaviour. The experimental data followed a very similar pattern to that plotted for propane. Lenoir (16) presented a closer study of this behaviour and the application of the phenomena to convergence pressures.

The equilibrium ratios plotted on Figure 20 for the experimental data show a more pronounced tendency toward the formation of an azeotrope. This tendency was most apparent for concentrations of hydrogen sulphide in excess of 75 mole percent. The tendency disappeared when the temperature was increased beyond the critical of mixtures containing more than 75 mole percent hydrogen sulphide.

The last group of figures also indicates a good correlation between the NGSMA data for normal butane and that presented for the normal butane - hydrogen sulphide binary. The largest discrepancy existed for the lowest temperature and the closest correlation was obtained for data in the critical region.



## F. CONCLUSIONS

1. Existing equipment was modified to make it more useful for studies of vapour - liquid equilibrium.
2. Vapour-liquid equilibrium data were obtained for the system hydrogen sulphide - normal butane at temperatures of  $125^{\circ}\text{F}.$ ,  $175^{\circ}\text{F}.$ ,  $200^{\circ}\text{F}.$ ,  $225^{\circ}\text{F}.$ , and  $275^{\circ}\text{F}.$
3. The critical locus for the system hydrogen sulphide and normal butane was determined. Equilibrium ratios were calculated for the system hydrogen sulphide - normal butane.
4. Comparisons of equilibrium ratios were made for hydrogen sulphide in binary systems with methane, ethane, propane, normal butane and normal pentane.
5. The system hydrogen sulphide - normal butane does not have any azeotropes in the vapour - liquid region, but it does have a tendency toward azeotropic behaviour.



## NOMENCLATURE

C	number of components
F	number of degrees of freedom
f	fugacity
$f^0$	fugacity in the pure state
K	equilibrium ratio
N	number of phases
P	pressure
$P_v$	vapour pressure
x	mole fraction in the liquid phase
y	mole fraction in the gas phase

### Subscripts

g	gas phase
i	component i
l	liquid phase



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APPENDIX I  
TABULATIONS OF EXPERIMENTAL  
RESULTS



TABLE I  
 VAPOUR-LIQUID EQUILIBRIUM DATA FOR THE  
 SYSTEM HYDROGEN SULPHIDE-NORMAL BUTANE  
 AT 125° F

PRESSURE psia	COMPOSITION - WEIGHT : FACTOR			
	G A S		L I Q U I D	
	H S 2	n-C H 4 8	H S 2	n-C H 4 8
78		1.00		1.00
102			0.035	0.965
128	0.045	0.595	0.096	0.904
144	0.460	0.540	0.118	0.882
160			0.150	0.850
201	0.635	0.365	0.247	0.753
214	0.633	0.357	0.262	0.738
234	0.688	0.312		
246			0.325	0.675
247			0.332	0.688
253	0.725	0.275	0.349	0.651
275	0.769	0.231		
282			0.399	0.601
312	0.811	0.189	0.469	0.531
392	0.877	0.123	0.631	0.369
419	0.891	0.109		
420			0.716	0.284
447	0.913	0.087	0.778	0.122
457			0.791	0.208
483	0.945	0.005		
487			0.862	0.138



TABLE 2  
 VAPOUR- LIQUID EQUILIBRIUM DATA FOR THE  
 SYSTEM HYDROGEN SULPHIDE -NORMAL BUTANE  
 AT 175° F

PRESSURE psia	COMPOSITION - WEIGHT FACTOR			
	G A S		L I Q U I D	
	H S 2	n-C H 4 8	H S 2	n-C H 4 8
291	0.525	0.475	0.184	0.816
411	0.680	0.320	0.364	0.636
477	0.749	0.251	0.465	0.535
627	0.840	0.160	0.692	0.308
741	0.900	0.100	0.810	0.190



TABLE 3  
 VAPOUR-LIQUID EQUILIBRIUM DATA FOR THE  
 SYSTEM HYDROGEN SULPHIDE-NORMAL BUTANE  
 AT 200° F

PRESSURE psia	COMPOSITION - WEIGHT FACTOR			
	G A S		L I Q U I D	
	H <sub>2</sub> S	n-C <sub>4</sub> H <sub>8</sub>	H <sub>2</sub> S	n-C <sub>4</sub> H <sub>8</sub>
340	0.431	0.569		
343			0.172	0.828
435	0.582	0.481	0.275	0.725
437			0.287	0.713
537			0.414	0.586
554	0.693	0.307		
654	0.770	0.230	0.520	0.480
683			0.560	0.440
768			0.674	0.326
853	0.854	0.146	0.767	0.233
990	0.906	0.094		
994			0.861	0.139
1060			0.920	0.080
1100	0.955	0.045		
1105			0.937	0.063
1139	0.985	0.015		



TABLE 4  
 VAPOUR-LIQUID EQUILIBRIUM DATA FOR THE  
 SYSTEM HYDROGEN SULPHIDE-NORMAL BUTANE  
 AT 225° F

PRESSURE psia	COMPOSITION - WEIGHT FACTOR			
	G A S		L I Q U I D	
	H <sub>2</sub> S	n-C <sub>4</sub> H <sub>8</sub>	H <sub>2</sub> S	n-C <sub>4</sub> H <sub>8</sub>
365	0.332	0.678	0.313	0.879
509	0.509	0.491	0.270	0.730
705	0.631	0.369	0.465	0.535
745	0.683	0.317		
785			0.540	0.460
930	0.784	0.216	0.709	0.291
1008	0.800	0.200	0.725	0.275
1050	0.812	0.188	0.785	0.215
1080			0.809	0.191



TABLE 5  
 VAPOUR-LIQUID EQUILIBRIUM DATA FOR THE  
 SYSTEM HYDROGEN SULPHIDE -NORMAL BUTANE  
 AT 250° F

PRESSURE psia	COMPOSITION - WEIGHT FACTOR			
	G A S		LIQUID	
	H <sub>2</sub> S	n-C <sub>4</sub> H <sub>8</sub>	H <sub>2</sub> S	n-C <sub>4</sub> H <sub>8</sub>
494	0.319	0.681	0.159	0.841
537	0.380	0.620	0.187	0.813
628	0.454	0.546	0.284	0.716
751	0.523	0.477	0.396	0.604
820			0.459	0.541
818	0.558	0.442		
907	0.581	0.419	0.530	0.470
931	0.588	0.412	0.541	0.459



TABLE 6  
 VAPOUR-LIQUID EQUILIBRIUM DATA FOR THE  
 SYSTEM HYDROGEN SULPHIDE-NORMAL BUTANE  
 AT 275° F

PRESSURE psia	COMPOSITION - WEIGHT FACTOR			
	G A S		L I Q U I D	
	H <sub>2</sub> S	n-C <sub>4</sub> H <sub>8</sub>	H <sub>2</sub> S	n-C <sub>4</sub> H <sub>8</sub>
624	0.265	0.735	0.184	0.816
630	0.273	0.727	0.191	0.809
706	0.337	0.663	0.265	0.735
761	0.364	0.636		
770	0.363	0.637	0.320	0.680
790	0.362	0.648	0.334	0.656



TABLE 7  
 EQUILIBRIUM RATIOS FOR THE SYSTEM  
 HYDROGEN SULPHIDE - NORMAL BUTANE  
 AT 125° F

PRESSURE psia	E Q U I L I B R I U M   R A T I O S	
	$H_2S$	$n-C_4H_8$
100	7.889	0.7427
200	2.735	0.4935
300	1.820	0.3710
400	1.327	0.3647
500	1.058	0.4693



TABLE 8

EQUILIBRIUM RATIOS FOR THE SYSTEM

HYDROGEN SULPHIDE - NORMAL BUTANE

AT 175° F

PRESSURE psia	E Q U I L I B R I U M R A T I O S	
	H <sub>2</sub> S	n-C <sub>4</sub> H <sub>8</sub>
200	4. 647	0. 7339
300	2. 753	0. 5782
400	1. 959	0. 5106
500	1. 508	0. 4920
600	1. 262	0. 5143
700	1. 145	0. 5417
800	1. 077	0. 5352
900	1. 014	0. 5000



TABLE 9  
 EQUILIBRIUM RATIOS FOR THE SYSTEM  
 HYDROGEN SULPHIDE - NORMAL BUTANE  
 AT 200  $^{\circ}$ F

PRESSURE psia	E Q U I L I B R I U M R A T I O S	
	$\text{H}_2\text{S}$	$\text{n-C}_4\text{H}_8$
200	9.0	0.9679
300	3.083	0.7159
400	2.218	0.5984
500	1.776	0.5521
600	1.530	0.5265
700	1.327	0.5340
800	1.147	0.6214
900	1.077	0.6804
1000	1.048	0.6866
1100	1.028	0.6389



TABLE 10

EQUILIBRIUM RATIOS FOR THE SYSTEM

HYDROGEN SULPHIDE - NORMAL BUTANE

PRESSURE psia	E Q U I L I B R I U M $\text{H}_2\text{S}$	R A T I O S $\text{n-C}_4\text{H}_8$
300	3.300	0.8532
400	2.207	0.7632
500	1.859	0.6822
600	1.560	0.6741
700	1.371	0.6791
800	1.260	0.6771
900	1.167	0.6949
1000	1.087	0.7612



TABLE 11  
 EQUILIBRIUM RATIOS FOR THE SYSTEM  
 HYDROGEN SULPHIDE - NORMAL BUTANE  
 AT 250° F

PRESSURE psia	E Q U I L I B R I U M R A T I O S	
	H <sub>2</sub> S	n-C <sub>4</sub> H <sub>8</sub>
400	2.441	0.8948
500	2.099	0.7876
600	1.709	0.7587
700	1.434	0.7706
800	1.253	0.8410
900	1.111	0.8787



TABLE 12  
 EQUILIBRIUM RATIOS FOR THE SYSTEM  
 HYDROGEN SULPHIDE - NORMAL BUTANE  
 AT 275<sup>o</sup> F

PRESSURE psia	E Q U I L I B R I U M R A T I O S	
	H <sub>2</sub> S	n-C <sub>4</sub> H <sub>8</sub>
450	1. 750	0. 973
500	1. 645	0. 946
600	1. 463	0. 910
700	1. 314	0. 893
750	1. 197	0. 916



APPENDIX #2CHARGING PROCEDURE

A standard procedure was followed to charge the cell. The best procedure is detailed below in step form. It should be noted that the least volatile component is charged first.

1. Evacuate the system for initial charge.
2. Connect the container holding the least volatile component to the sample pump outlet.
3. Cool sample pump below room temperature or warm the sample container.
4. Evacuate lines between cell and sample along with the sample pump.
5. Allow liquid sample to enter pump until pump contains desired charge.
6. Close valve separating sample container from the sample pump.
7. Open valve to cell and pump in charge. Close the valve.
8. To avoid loss of any sample purge system with mercury until further sample does not enter cell when sample pump forces mercury into the cell.
9. Connect container for next component and repeat steps 3 to 8.



APPENDIX #3SAMPLING PROCEDURE

Many different methods of sampling were attempted. The best of these are detailed in step form below for both gas and liquid samples. It should be noted that the volumes of sample given are approximate. The actual volume required depends on the temperature and pressure of the cells contents.

**A. LIQUID SAMPLE**

1. Evacuate the sample pump.
2. Take about 0.6 cc. of pure mercury into the pump.
3. Make sure the liquid phase is at the sample port.
4. Purge the sample line with mercury from the sample pump.
5. Remove approximately 0.4 cc. of sample from the cell while adding an identical volume of mercury with the displacement pump.
6. Cover the window with mercury using the double acting pump.
7. Remove approximately 0.6 cc. of mercury through the sample pump while adding an identical volume to the cell with the displacement pump.
8. Isolate the sample pump.
9. Expand the sample to 2 cc. in the sample pump.
10. Carefully expand the sample to a gas burrett from the sample pump.
11. Analyse the sample in chromatograph.



## B. GAS SAMPLE

1. As for liquid sample.
2. As for liquid sample
3. Make sure gas phase is at sample port
4. As for liquid sample.
5. Remove approximately 1.5 cc. of sample from the cell while adding an identical volume of mercury to the cell with the displacement pump.
6. Isolate the sample pump.
7. Expand the sample from the sample pump to a gas burrette.
8. Analyse the sample in chromatograph.









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